O.I. VOROBYOVA, K.M. DUNAEVA, E.A. IPPOLITOVA,
and N.S. TAMM

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TO THE READER

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PREFACE

Practical Inorganic Chemistry is aimed at assisting students to systematically study the basic properties of the chemical elements and their compounds from the standpoint of D. Mendeleev's Periodic System and also to gain skill in performing laboratory experiments. The textbook covers the most important sections of general and inorganic chemistry.

Substantial changes have occurred in organizing laboratory work in inorganic chemistry during the last decades. Great attention is being given to modern preparative techniques. Students using the present textbook will acquaint themselves with procedures of work in a modern laboratory. The latter include the carrying out of operations in vacuum, synthesis in non-aqueous solvents, the conducting of reactions in a gaseous medium (a fluidized bed, "transport" reactions) or in liquefied gases, photolytic reduction and oxidation, and the preparation of pure substances (sublimation, recrystallization, extraction, chromatography, and distillation). Students will acquire skill in handling glass and quartz ware on standard joints, cryostats, thermostats, "dry" chambers, and simple measuring instruments.

The first chapter of the book includes sections that describe in detail the procedures for dehydrating organic solvents and drying solids, the fundamental principles of operation of vacuum installations and the technique of vacuum measurement, and work with chemical ware using joints. How to assemble apparatuses used most frequently in a laboratory is described in detail. This chapter also describes working procedures (the handling of electrical furnaces, temperature control, etc.) which, although being simple, are exceedingly important for students who are beginning to work independently in a chemical laboratory.

The present book devotes a lot of space to the synthesis of the most important inorganic compounds and the chemistry of the elements. Since the book contains a large number of experiments and syntheses, they cannot be performed by the students during the time allotted for practical work, and the authors have divided the laboratory works of each chapter into two parts. The first describes the obligatory experiments, and the second, supplementary experiments and syntheses.

The large number of diverse syntheses in the book enable the instructor to vary the assignments to the students and thus expand their chemical outlook.

Modern inorganic chemistry is a quantitative science. Consequently, when performing experimental work, students must determine the yield of the substances obtained and certain constants such as the boiling points, solubility, and cryohydrate points, and also perform the required calculations with the use of the fundamentals of thermodynamics.

Appendix 1 presents numerous reference tables containing most important data on the solubility of inorganic compounds in water, the density, dissociation constants, solubility products, ionization potentials of various atoms, etc., as well as thermochemical constants because many laws of inorganic chemistry cannot be explained without these quantities.

The book presents no theoretical explanations, but does contain many questions relating to the technique of an experiment and its theory. The student must answer them, using the relevant textbooks and supplementary literature, and also the materials of lectures. The need to find an answer to a question in the book will teach a student studying inorganic chemistry to work independently and thoughtfully with chemical literature from his very first steps, and, in addition, will relate the theoretical course and experimental work, which will help mastering the subject as a whole.

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1 WORK IN A LABORATORY AND TECHNIQUE OF AN EXPERIMENT

1.1 PROCEDURE OF WORK IN A LABORATORY

1. Work in a chemical laboratory is effective only when it is performed conscientiously, with an understanding of its theory. Moreover, every chemical operation requires that the experimenter be careful and attentive. Even an experiment that seems to be quite harmless may result in serious consequences when it is planned improperly. This is why students are allowed to work in a laboratory only after preliminary briefing.

A student must read the description of the experiments he is to perform in the guide to the practical work, acquaint himself in textbooks with the properties of the substances being studied, with the theory relating to the given topic, write the reaction equations, perform the required calculations, and also note the experiments that demand special attention and carefulness.

The present guide contains a description of a large number of synthesis experiments requiring quite complicated equipment. Before beginning such an experiment, the student must think it out thoroughly as a whole, compile a concise plan of the operations to be performed consecutively, and understand the purpose of each component of the apparatus. All the pieces of equipment in which experiments are run must be assembled compactly, suitably, and attractively.

2. Every student is given a permanent place in the laboratory (a working table and locker for laboratory ware), and he must keep it clean and in good order. Only the objects needed at the given time for work must be on the table.

3. Put the reagents needed for work on the shelves above the laboratory tables or on special shelves. Concentrated acids and odorous substances are an exception. Store them in fume cupboards.

4. Never leave reagents taken from the shelves at your place of work.

5. Take dry reagents with a clean spatula or a special spoon. When pouring solutions from bottles, hold the latter with the labels upward (to prevent soiling them).

6. If the guide does not indicate what amount of a substance must be taken for performing an experiment in a test tube, take a dry substance in an amount covering the bottom of the tube, and a solution in an amount not more than one-sixth of the tube volume.

7. Never pour unconsumed reagents back into their storage bottles. Hand them in to the laboratory assistant.

8. Put caps and stoppers of reagent jars and bottles with their surface that was not in contact with the reagent on the table.

9. Never perform experiments not described in the guide without the instructor's permission.

10. Use only distilled water when preparing aqueous solutions, washing precipitates with water, rinsing glass ware, and so on.

11. Always wear overalls when working in a laboratory.

12. Hand in all synthesized substances to the instructor. Indicate the composition and weight of the preparation, and also your name and the date on the label.

LABORATORY NOTEBOOK

Enter all your observations of the experimental work and conclusions in a laboratory notebook that is a document reflecting all your work. Write your surname, initials, class number and the name of the course on the cover or first page of the notebook. Make all entries only in ink, concisely, accurately, and legibly, directly after performing an experiment. The writeup must contain the following information:

1. The date of performing the work.
2. The names of the topic and experiment.
3. A description of the conditions of the experiment.
4. A drawing or diagram of the apparatus used.
5. The equations of all the reactions proceeding in the experiments.
6. The change in the colour of the substances, the separation and nature of a precipitate.
7. The calculations made in performing the work.
8. Answers to the questions contained in the guide.
9. Conclusions.

It is good to use a large squared notebook for your laboratory record.

An example of a writeup of an experiment in a laboratory notebook is given below:

Date : October 15, 1985 Name of experiment	Topic: Bromine. Preparation and running of experiment	Observations. Conclusions
Preparation of bromine by oxidizing hydrobromic acid by manganese(IV) oxide	Drawing of apparatus. Reaction equations. Required calculations. Tabulated data (b.p. of bromine, density, etc.)	When the reaction mixture is heated, a brown bromine vapour condensing as a heavy reddish brown liquid evolves

Enter the first and partly the second column when preparing for the experiment. Fill in the third column in the laboratory when running the experiment. The passive voice is preferred for the writeup.

SAFETY

1. Perform all work with substances that are poisonous or have an unpleasant odour, and also the evaporation of acids and acidic solutions only in a fume cupboard; work far from a flame with flammable substances.
2. Beware of water when working with metallic sodium and other alkali metals. Hand in trimmings of these metals to the laboratory assistant. Never throw them into the containers for waste.
3. When heating solutions in a test tube, always hold it with its opening away from yourself and from your neighbour at the working table. It is especially important to observe this rule when concentrated acids or solutions of alkalies are being heated. It is good to perform these experiments in a fume cupboard.
4. Never bend over a liquid being heated or substances being fused to avoid splashes getting onto your face.
5. Never inhale odorous substances including evolving gases by bending closely over a vessel with these substances. Direct a stream of air from the vessel opening toward yourself by waving your hand slightly and carefully smell it.
6. When working with solid alkalies (the crushing of large lumps, the filling of desiccators with an alkali, the preparation of mixtures for fusion, etc.), wear eye protection. Handle the alkali only with a spatula, tong, or pincers. Carefully remove all surplus alkali from your workplace. Observe the same safety measures when working with phosphorous anhydride.
7. When diluting concentrated acids, especially sulphuric acid, pour the acid into water, and not vice versa.
8. Work with mercury on special trays with high sides.
9. Pour the residues of mercury and arsenic compounds, metal cyanides, or compounds of the rare and valuable metals into special jars (take them from the laboratory assistant).
10. Before washing glass ware containing residues of white or red phosphorus, immerse it into baths with a solution of copper sulphate (take them from the laboratory assistant).

FIRST AID

1. If a concentrated acid (sulphuric, nitric, acetic, etc.) gets on your skin (hands, eyes, etc.), immediately wash the burnt spot with a strong stream of water for three to five minutes, after which apply a cotton wool bandage wetted with an alcohol solution of tannin or

a 3% potassium permanganate solution. If burns are strong, after first aid immediately see a physician.

2. If your skin has been burnt by an alkali solution, wash the burnt spot with water until the skin stops feeling slippery, after which apply a bandage wetted with an alcohol solution of tannin or a 3% potassium permanganate solution.

3. If splashes of an acid or alkali get into your eyes, immediately wash them with a great deal of water at room temperature, and then see a physician without delay.

4. If you have burnt your skin with a hot object (glass, metals, etc.), first apply a bandage wetted with an alcohol solution of tannin or a potassium permanganate solution, and then a greasy bandage (an ointment for burns).

5. When burnt by phosphorus, apply a bandage wetted with a 2% copper sulphate solution to the burnt spot.

6. If a solution of hydrofluoric acid gets on your skin, wash the burnt spot with running water, and then apply a cotton wool bandage wetted with a 10% solution of calcium chloride or a saturated solution of magnesium sulphate.

7. If someone in your class has been poisoned by chlorine, bromine, hydrogen sulphide, or carbon monoxide, take him or her out into the open air and immediately call a physician.

8. If you have been poisoned by an arsenic or mercury compound, or by a cyanide, immediately see a physician. The precautions to be taken when working with other poisonous substances are indicated in the relevant sections of the book.

LABORATORY WARE

Experiments are performed in special laboratory ware made from thin or thick laboratory glass. Thin glassware must be chemically and thermally stable. Ware in which reactions are performed with heating is made from heat-resistant Pyrex glass and quartz.

Pyrex glass contains about 80% of silicon dioxide, about 5% of alkalies, and has a low expansion coefficient. Ware made from it has a high thermal stability. The softening point of this glass is about 620 °C.

Laboratory ware for reactions requiring a higher temperature is made from quartz glass. It contains about 99.95% of silicon dioxide and is distinguished by a high thermal stability and by its inertness with respect to a number of chemical reagents (except for hydrofluoric and phosphoric acids). The softening point of quartz glass is about 1650 °C.

The glassware shown in Fig. 1 is used the most in chemical laboratories. It includes test tubes (*1a*), Wurtz test tubes (*1b*), beakers *2*, flat-bottomed flasks *3*, round-bottomed flasks *4*, Wurtz flasks *5*, coni-

cal (Erlenmeyer) flasks *6*, side-arm bottles (for suction) *7*, crystallizers *8*, funnels *9*, desiccators *10*, weighing bottles *11*, extractors *12*, calcium chloride tubes *13*, tees *14*, adapters *15*, U-tubes *16*, dephlegmators (reflux condensers) *17*, coolers *18*, wash bottles (*19a*) and dry-

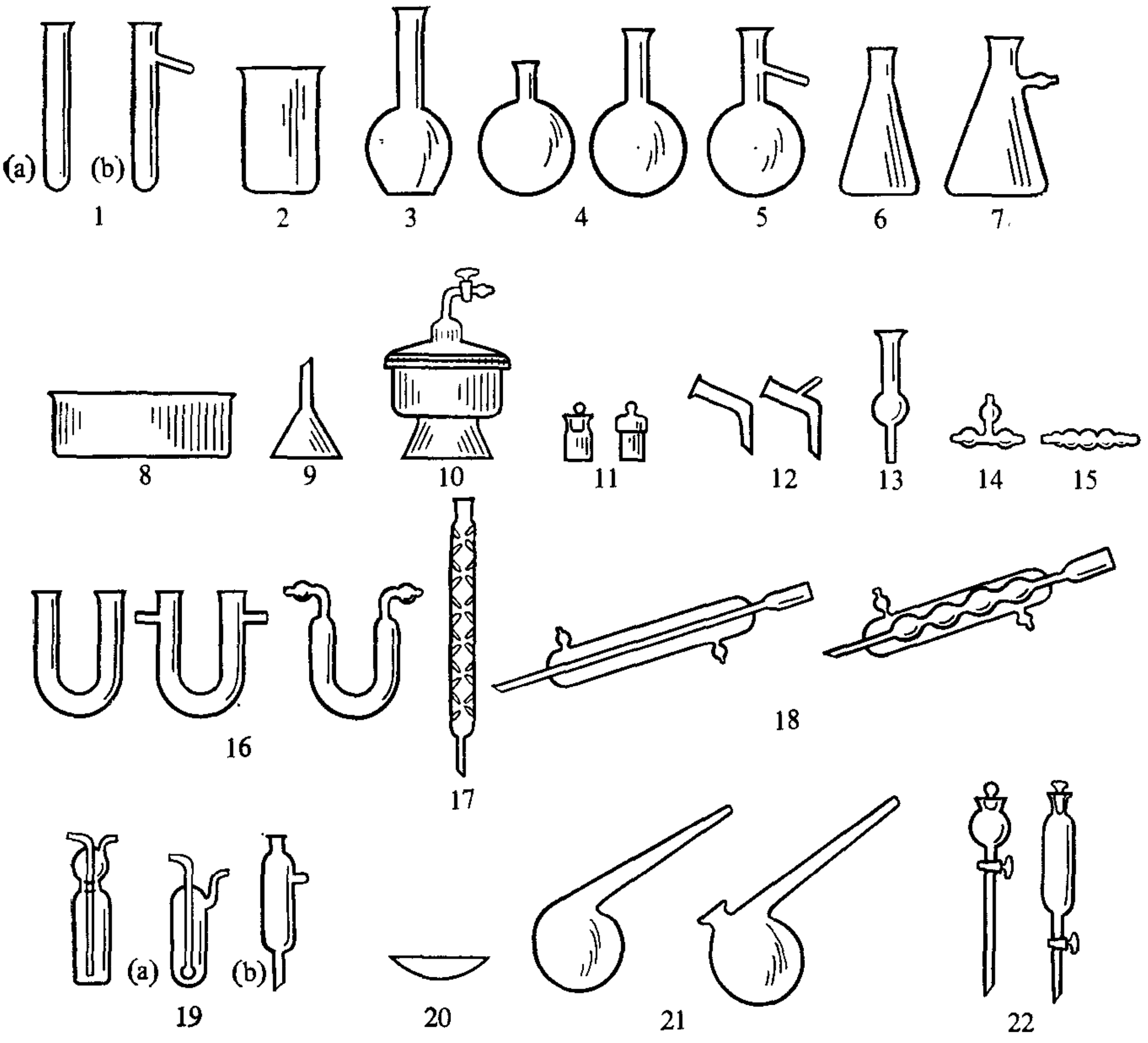


Fig. 1. Glassware

ing columns (*19b*), watch glasses *20*, retorts *21*, and dropping funnels *22*.

In addition to glassware, porcelain ware is also used in the laboratory (Fig. 2): bowls *1*, cups *2*, crucibles with lids *3*, Büchner funnels *4*, mortars and pestles *5*, boats *6*, and triangles *7*.

For working with small amounts of substances, laboratory ware of a small size and capacity is used, for example, 2- and 10-ml flasks, 20-, 10-, and 5-ml beakers, etc.

Measuring Vessels. The following measuring vessels (graduates) are generally used in laboratory work in inorganic chemistry: flasks, pipettes, burettes, and measuring glasses.

Measuring flasks (Fig. 3) are used to prepare a solution with an exact concentration. They are flat-bottomed flasks with a long and narrow neck on which a thin line is marked. This mark indicates the boundary of a liquid which at a definite temperature occupies the volume indicated on the flask. Since the neck of the flask is narrow,

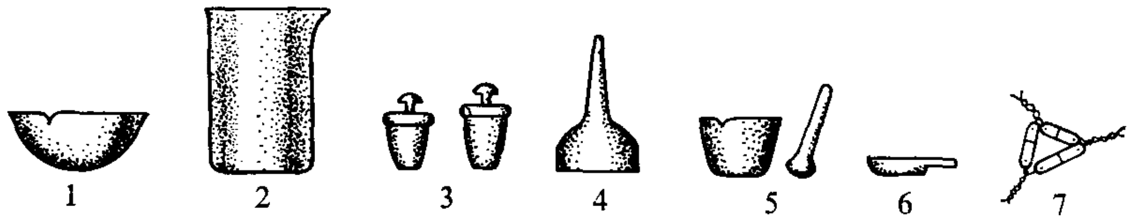


Fig. 2. Porcelain ware

a comparatively slight change in the volume of the liquid in the flask appreciably changes the position of its meniscus. Measuring flasks have ground-glass stoppers. Usually, flasks for 50, 100, 250, 500, and 1000 ml are employed.

Pipettes are used for the exact measurement of a definite volume of a liquid. They are narrow cylindrical glass tubes with still narrower top and bottom ends (Fig. 4*a*). The upper part of an ungraduated pipette has a mark showing up to what level it must be filled to obtain the volume indicated on it. Pipettes with a volume of 10 or 20 ml are used the most. Graduated pipettes are also used (Fig. 4*b*).

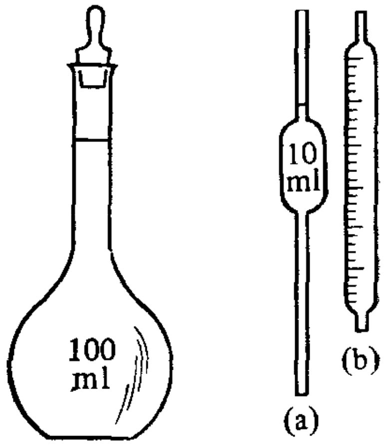


Fig. 3. A measuring flask
Fig. 4. Pipettes

Burettes (Fig. 5) are intended for pouring out strictly definite volumes of a liquid. They are long glass tubes with a graduated scale. The most popular are 50-ml burettes graduated by tenths of a millilitre. The bottom part of a burette is provided with a stopcock. The simplest burettes have a valve consisting of a closely fitting glass bead within a short length of a rubber tube instead of a stopcock.

Graduated cylinders and glasses (Fig. 6) are used for the rough measurement of liquids and have various capacities, namely, 5, 10, 25, 50, 100, 150, 250, 500, 1000, and 2000 ml.

Ware Washing. Thoroughly wash laboratory ware before using it in an experiment. First rinse it with tap water. If the dirt is not removed, use a special test-tube brush. Never wash ware with water and sand because scratches may appear on the glass that detract from its strength.

Dirt can also be removed chemically by washing the ware with a chromium mixture*. This ensures good wettability of the glass. After washing the ware, pour the chromium mixture back into its bottle (but not into a sink), thoroughly wash the ware with tap water,

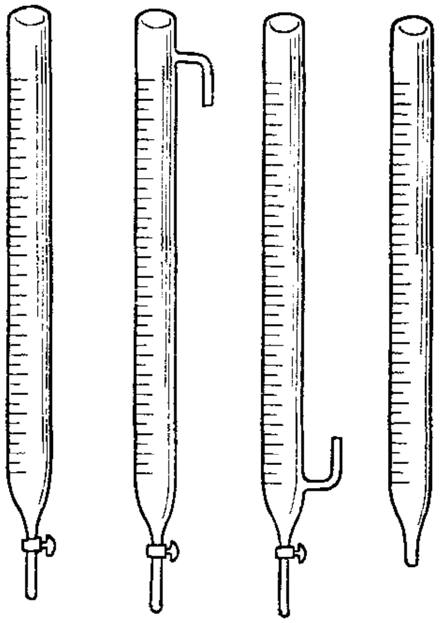


Fig. 5. Burettes

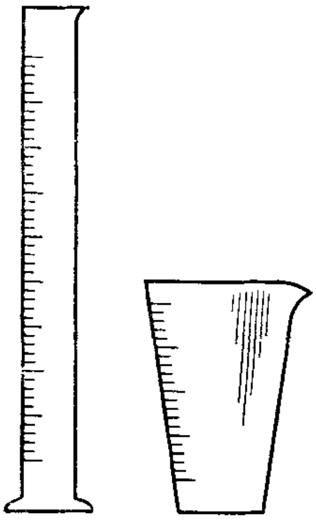


Fig. 6. A measuring cylinder and glass

and then rinse it two or three times with distilled water. Sometimes, an alcohol solution of an alkali is used for washing ware**.

Never wipe the inside of laboratory ware with a towel. When required, dry ware in a drying cabinet (except for measuring vessels, which are never dried by heating).

HEATING EQUIPMENT

A variety of heating equipment is used in a laboratory, namely, gas burners, plates, baths, furnaces, drying cabinets, etc.

Burners. The most convenient one is the *Teklu burner* (Fig. 7*a*) because its design enables one to regulate not only the inflow of air, but also that of gas. The latter enters the base of a Teklu burner via side connection *1*, whence it passes along narrow tube *2* into tapered tube *3*, where it mixes with air. In addition to a gas cock, the supply of gas can also be regulated by screw *4*. Air enters the

* Prepare a chromium mixture in a large porcelain mortar. Triturate about 10 g of potassium bichromate, wet it with 3-5 ml of water, and add 100 ml of a 96% sulphuric acid solution while stirring. Transfer the settled solution into a thick-walled bottle with a ground-glass stopper.

** Prepare an alcohol solution of an alkali by dissolving 5-10 g of sodium hydroxide in 10 ml of ethyl alcohol.

burner via the slot between tube *3* and disk *5* mounted on a screw thread. By turning the disk, one can change the width of the slot and thus control the flow of air into the burner.

Air enters a *Bunsen burner* (Fig. 7*b*) through orifice *1* in the lower part of the upper tube. The opening of this orifice can be controlled by rotating sleeve *2* provided with a mating orifice.

The greatest amount of heat is obtained in complete combustion of the gas, when the flame is non-luminous. When the supply of air is reduced, the flame becomes luminous and smoky. To ignite a burner, shut off the access of air to it, light a match, open the gas cock, and after one or two seconds apply the lighted match to the edge of the burner opening. Make the flame non-luminous by increasing the inflow of air.

How can the luminosity of a flame be explained? Acquaint yourself with the different zones of a non-luminous flame (Fig. 8). Which zone of the flame is the hottest?

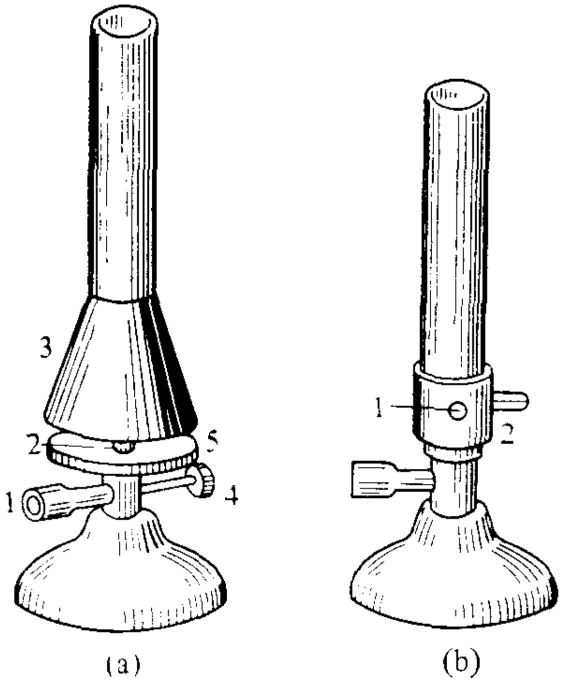


Fig. 7. Teklu and Bunsen burners

In the lighting of a burner with an open air inlet, the flame may "jump" into the burner. Such a flame becomes luminous and smoky. The burner gets very hot, which may lead to serious consequences such as ignition of the rubber tubing through which the gas is supplied, spoiling of the table, and burning of one's hands. In addition, incomplete combustion of the gas results in a large amount of carbon monoxide. If in the course of work the flame jumps into the burner,

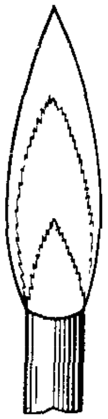


Fig. 8. Zones of a non-luminous flame

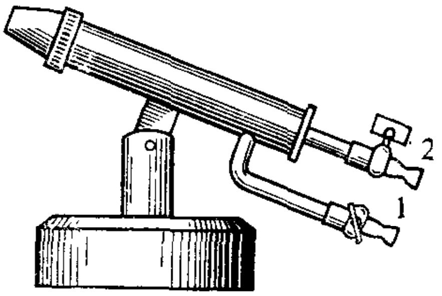


Fig. 9. A brazing burner

shut the gas cock, let the burner cool, and light it again as indicated above.

A brazing burner (Fig. 9) is used to obtain a flame with a higher temperature. It differs from a conventional burner in that its bottom part has two tubes with cocks. Air is fed into the burner via tube *1*, and gas via tube *2*. Air is supplied into the burner by a motor-driven blower, or it is fed in via a special air pipe from a central compressor plant. By regulating the supply of air and gas, you can obtain a flame of a various height and temperature.

Prior to lighting a burner, see that all the cocks on the main gas and air pipes, and also at the burner are shut. First open the air cock at the burner to the limit, and then the gas cock. Apply a lighted match to the mouth of the burner from a side (do not bend over it), and the gas will ignite in a wide smoky flame (there is no blast because the cock on the main air pipe is shut). Turn the gas cock to reduce the supply of gas. Next by smoothly turning the cock on the air pipe, set a normal blast (without breaking away of the flame). By sequentially turning the air and gas cocks at the burner, regulate the flame until it becomes uniform and sharp with a light blue colour and without any indications of soot. When the blast is too strong, the flame will break away from the burner mouth. If the flame jumps into the burner, immediately close the gas cock, and light the burner again in about 1.5 minutes.

The part of a flame beginning directly at the mouth of the burner is called the first reducing zone (300-520 °C). It is followed by the second zone, of complete combustion (1540-1560 °C). The third, oxidizing zone, is in direct contact with the oxygen of the air (~ 1540 °C). The heating of glass should be performed at the boundary between the second and third zones.

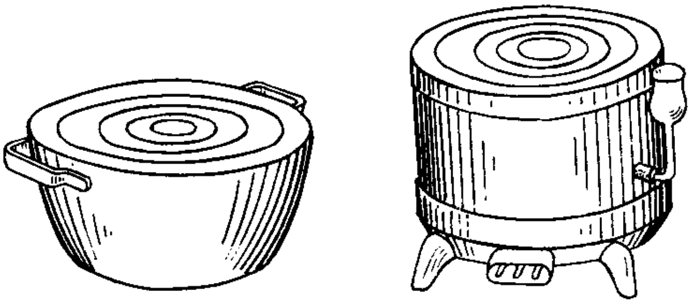
Extinguish the flame as follows. First shut the air pipe cock, next the gas pipe cock, then shut the gas and air cocks at the burner. Never close the gas cock first because in this case the flame will immediately extinguish, and the gas remaining in the tubing and the burner will enter the premises.

Keep burners clean. See that nothing gets into the burner tube. Screw apart and clean burners from time to time.

Baths. A variety of baths are used for heating within a temperature interval from 100 to 300 °C.

A *water bath* is a metal vessel covered on top with a number of concentric flat rings fitting onto one another (Fig. 10*a*). The vessel is filled with water up to two-thirds of its volume, covered with the rings, and placed on a tripod. The water is heated up to boiling and constantly kept in this state by using a small flame of a gas burner. The vessel (bowl, beaker) with a solution to be heated is placed on the bath after removing enough rings for the vessel to be stable. See that the bath always contains water. Water baths with electric heating

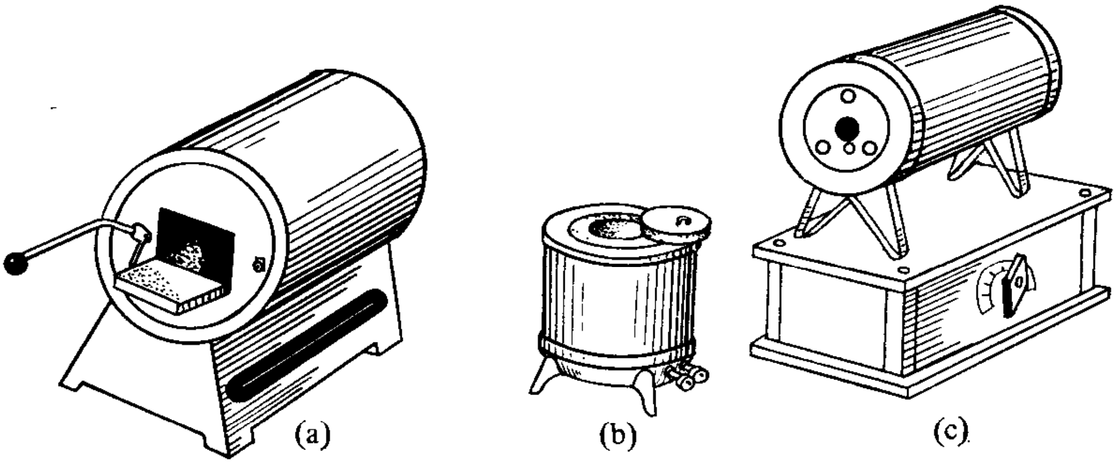
(Fig. 10*b*) are also used in laboratories. To obtain higher temperatures, oil or a concentrated solution of a salt (sodium or calcium chloride) is poured into the bath instead of water. In this case, enamelled baths are recommended.



(a) (b)

Fig. 10. **Baths:** *a*—water; *b*—water with electric heating

A *sand bath* is used for careful heating to high temperatures (200-300 °C) and is often a pan or iron tray with clean, well roasted sand. The bath is heated by the flame of a gas burner. At present, electrical sand baths are mainly used in laboratories.



(a) (b) (c)

Fig. 11. Furnaces: *a*—muffle; *b*—crucible; *c*—tube

Furnaces. Electrical furnaces are used for heating or roasting substances at a high temperature.

In a muffle or crucible furnace (Fig. 11*a* and *b*), substances are roasted in crucibles.

A *tube furnace* (Fig. 11*c*) is used to heat a reaction mixture in refractory tubes (quartz, porcelain, etc.). The preparation is placed in a boat (porcelain, quartz, platinum, etc.) that is pushed with a glass rod into a quartz or porcelain tube in the furnace.

Remember that the laboratory electrical furnaces can be intended for a voltage of either 220 V or 127 V in the mains. Prior to connecting an electrical furnace to the mains, check the voltage (indicated on the furnace) for which it is intended.

1.2 TECHNIQUE OF LABORATORY WORK

TEMPERATURE CONTROL

Heating equipment (furnaces and drying cabinets) often contains *rheostats* that can be used to roughly maintain the required temperature.

Autotransformers are also widely used in laboratories. They allow the temperature to be controlled within a narrower interval. Let us consider a type ЛАТР-1 autotransformer (Fig. 12). Its front panel has six terminals. It is connected to 220-V mains via terminals *1* and *3*,

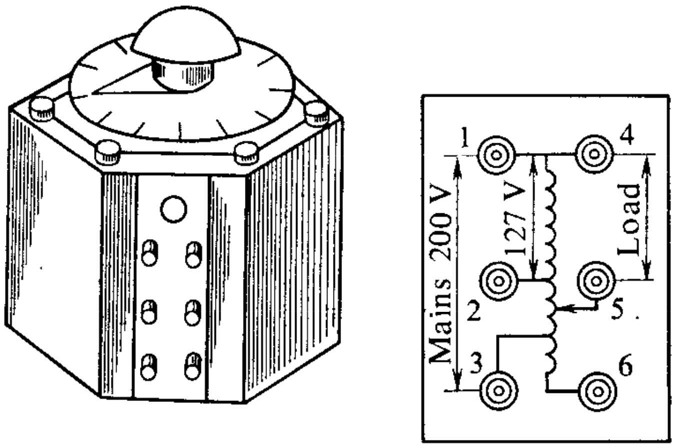


Fig. 12. A laboratory autotransformer

or to 127-V mains via terminals *1* and *2*. A furnace in both cases has to be connected to terminals *4* and *5* ("Load") of the autotransformer.

The upper panel of the autotransformer has a scale graduated from 0 to 250 V, and a handle provided with a pointer. Turning of the handle changes the voltage of the current in the furnace winding and thus sets the required temperature. Connect a furnace to the mains via an autotransformer as follows: place the pointer on the upper autotransformer scale opposite the zero graduation, next connect the furnace to it and connect the autotransformer to the mains in accordance with their voltage.

TEMPERATURE MEASUREMENT AND HEATING PROCEDURES

Thermometers. Conventional mercury thermometers are used to measure temperatures not exceeding 300 °C. Special thick-walled glass thermometers make it possible to determine temperatures up to 500 °C.

Thermocouples (Thermoelements). High temperatures are usually measured with thermocouples connected to millivoltmeters having

a double scale. The upper row of figures gives the readings in millivolts, and the lower one, in degrees Celsius.

A thermocouple consists of two wires of dissimilar metals or alloys insulated from each other by placing them in a two-channel porcelain tube. The wires are welded together at one end (the hot or measuring junction of the thermocouple) (Fig. 13). The free ends of the wires are connected to the terminals of a millivoltmeter (the cold or reference junction of the thermocouple). If the hot and cold junctions of the thermocouple are at the same temperature, there is no current in the circuit, and the galvanometer pointer is at zero. If the measuring junction is heated, a current arises in the circuit, and the instrument pointer moves along the scale and indicates the temperature difference between the measuring junction and the reference one. The temperature of the measuring junction is found by adding this difference to the temperature of the reference junction (room temperature, the temperature of melting ice or of the vapour of boiling water).

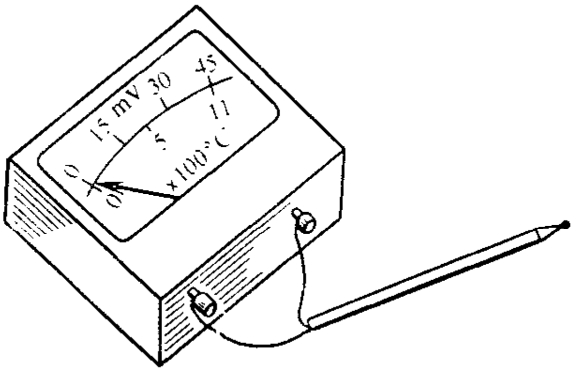


Fig. 13. A thermocouple

To measure temperatures not exceeding 800 °C, one should use thermocouples made from copper and constantan (the latter is an alloy of 45-60% copper, 40-55% nickel, and 0-1.4% manganese; it usually also contains about 0.1% carbon), Alumel (an alloy of 95% nickel, 2 % aluminium, 2% manganese, and 1% silicon), and Chromel (90% nickel and 10% chromium), or iron and constantan. Platinum-platinum/rhodium thermocouples are generally used for measuring high temperatures (up to 1600 °C).

For accurate temperature measurements, the reference ends of a thermocouple are maintained at a constant temperature, for example at that of melting ice or the vapour of boiling water. The temperature of a heated body (tube, ceramics, furnace) can be determined

Table 1. THE GLOW OF SOLIDS

Temperature, °C	Glow	Temperature, °C	Glow
500-600	dark red	1000-1200	white
600-800	cherry red	Above 1500	bright white
800-1000	yellow		

approximately according to its glow. Most solids when heated begin to emit hardly visible light at about 400-500 °C (Table 1).

Heat liquids in flasks, beakers, and porcelain bowls through asbestos gauzes. When heating alkaline solutions, you will find it good practice to introduce pieces of porous ceramics or glass capillaries soldered at one end into them.

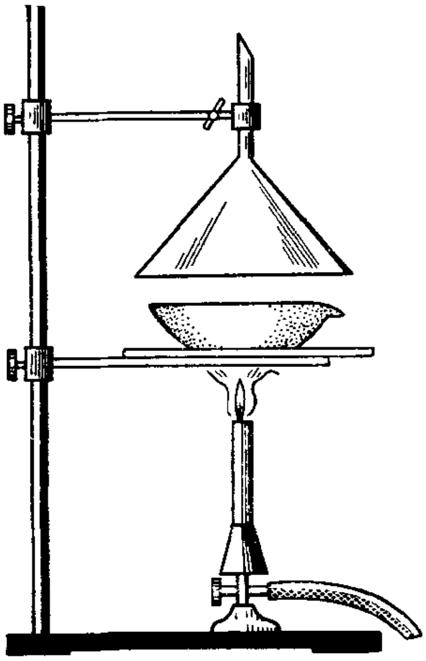


Fig. 14. Evaporation of a solution

To protect a liquid being heated from contamination, cover the beakers with watch glasses. When evaporating solutions (in bowls or beakers), funnels secured above the liquid being heated will serve the same purpose (Fig. 14).

When heating test tubes with small amounts of solutions and liquids with precipitates, secure the tube in a wooden holder or in a clamp of a stand in a slightly inclined position (see that the mouth of the tube is directed away from you and your neighbours). Carefully, using a small burner flame, heat the entire tube (*never heat the holder*!), next bring the top layer of the liquid up to its boiling point and, lowering the flame, gradually boil the entire contents of the tube. You can also heat a tube gripped in a holder while continuously shaking it with your hand.

When heating solids in a test tube, secure it in a clamp of a stand in an inclined position so that the mouth of the tube will be somewhat lower than its bottom (why?). First slightly heat the entire tube, and then more strongly the part where the solid is.

FILTRATION

To separate solids from a liquid, filtering through paper filters (smooth or fluted) is employed. Cotton wool, asbestos fibres, glass wool, crushed coal, porous glass, and a number of other materials can also be used as filters. The liquid separated in filtration is called the *filtrate*.

To prepare a smooth filter, take a square piece of filter paper corresponding to the size of the funnel to be used, fold it in half as shown by the dashed line in Fig. 15*a*, and then fold it in half another time. Cut away the outer corners along an arc. Insert the cone obtained into the funnel and wet it with distilled water. See that the entire surface of the filter adheres to the filter walls. The edge of the

filter must be lower than the funnel edge by at least 0.5 cm. There must be no air bubbles between the filter and the funnel.

To make a fluted paper filter, proceed as follows (see Fig. 15*b*). Take a round piece of filter paper and fold it into quarters; then

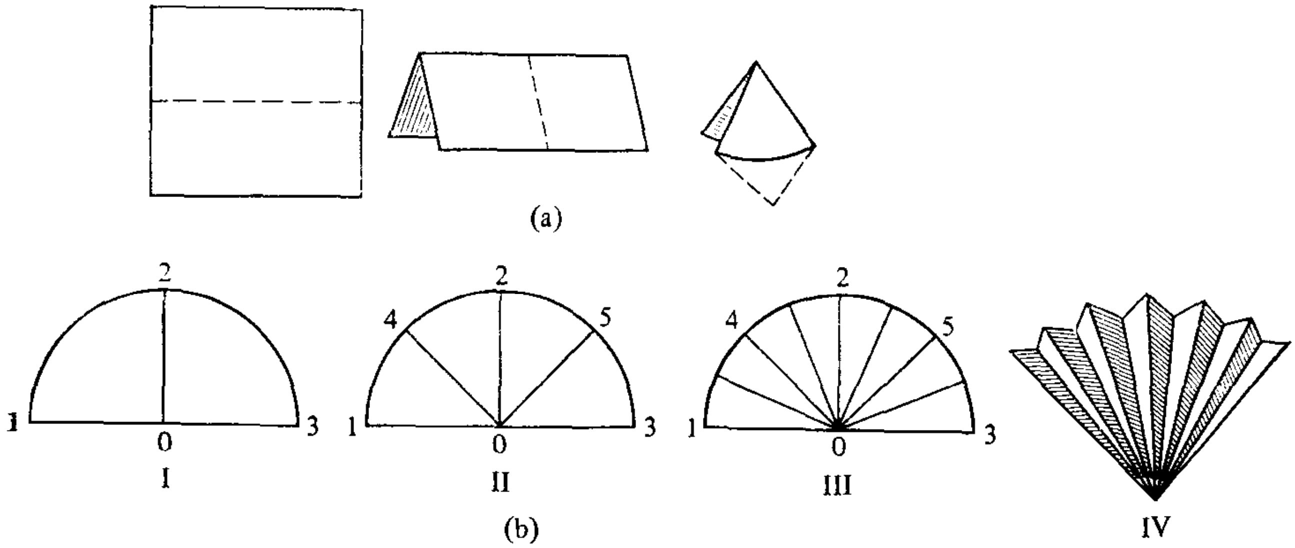


Fig. 15. Preparation of a filter

open it as shown in Fig. 15*b*, I. Place *01* along *02* and crease the paper, then open it. Put *03* along *02*, crease, and open. The result of these two operations is shown in Fig. 15*b*, II. Similarly, place *1* on *4*, crease and open, then *1* on *5*, *3* on *5*, and *3* on *4* (Fig. 15*b*, III). Next, making opposite folds, put *01* under *06*, crease, hold shut as you put *06* under *04*, and so on to make a fan by means of eight opposite folds. Open, and you have the fluted filter shown in Fig. 15*b*, IV.

Place a funnel with a filter in the ring of a stand so that its lower end is in contact with a wall of the receiver (why?). Pour the liquid to be filtered into the funnel along a glass rod (Fig. 16) which you should hold in your left hand.

Filtration can be accelerated by using funnels with ribbed walls (Fig. 17*a*) or with a long tube having a loop (Fig. 17*b*). A filter fits tightly against the upper edge of the funnel and the ribs, which ensures more rapid flowing down of the liquid and a small vacuum. In the second case, the loop plays the role of a siphon, when it is filled, the liquid rapidly flows down, and a rarefied space forms in the tube.

In the recrystallization of substances, hot saturated solutions usually have to be filtered. The solution cools during filtration, and the substance, crystallizing on the filter, hinders the process. This results in a great loss of the substance being crystallized. To avoid such losses, it is good practice to filter hot solutions in a glass funnel with a short cut off tube that is placed in a device with electrical (Fig. 18*a*) or water (Fig. 18*b*) heating. A device with water heating has double walls with water between them. The water is heated to

boiling in a side arm. A fluted filter is placed in the glass funnel. With such filtration, virtually no crystallization occurs on the filter.

For the more rapid separation of insoluble substances, filtration under reduced pressure is performed (Fig. 19). A porcelain Büchner

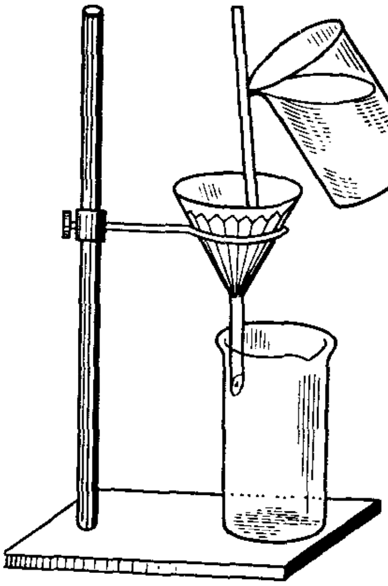


Fig. 16. Filtration

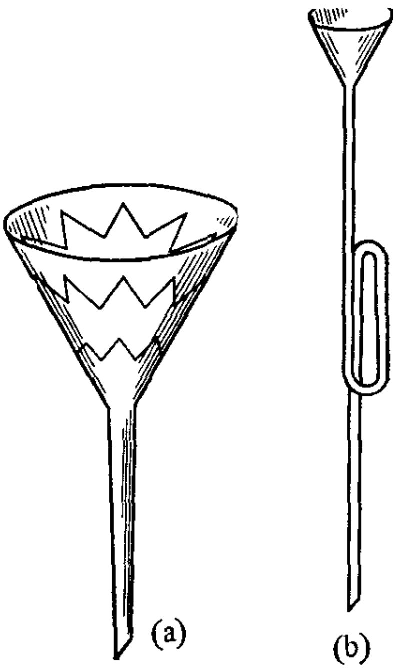


Fig. 17. Accelerated filtration

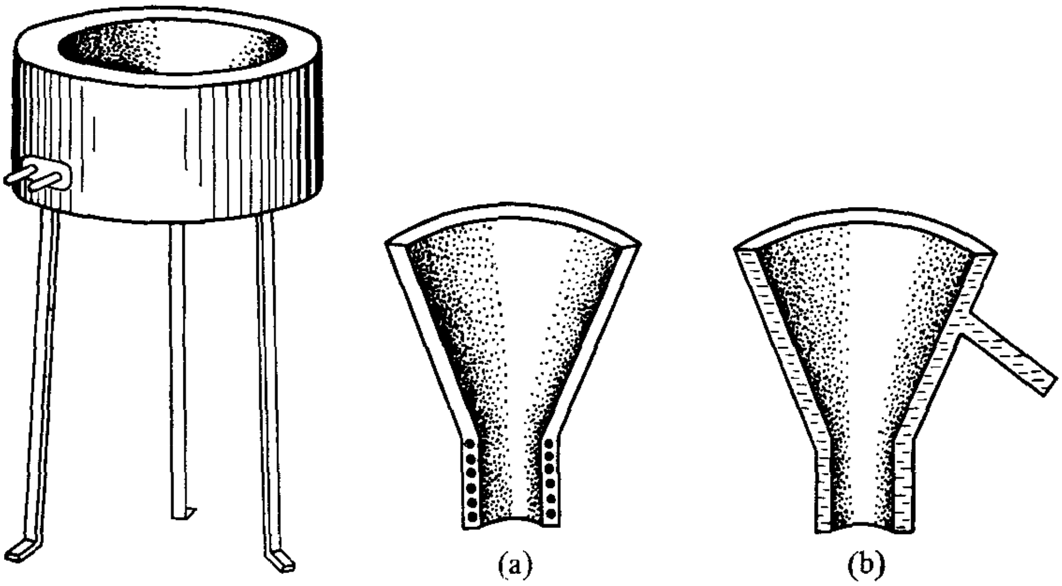


Fig. 18. Devices for heating funnels: *a*—with electric heating; *b*—with water heating

funnel (or a funnel with a glass filtering bottom) is inserted through a stopper into a thick-walled flask for suction out. A rarefaction is produced by a water-jet pump or the vacuum line of the laboratory. There must be an empty protective bottle between the suction flask and the pump (why?).

Put two paper filters on the bottom of the Büchner funnel. The lower one must be of the same size as the funnel bottom, while the diameter of the upper one must be 0.5 cm larger than that of the first one. To cut out such circles, put a sheet of filter paper on the funnel and slightly press it down with your palm. By cutting the filter paper along the imprint, obtain the upper (larger) filter. Cut out the smaller filter, place it on the bottom of the funnel, wet it with a small amount of distilled water, and press it against the bottom. Put the second filter on top and fold its edges onto the filter walls. Connect the device to a pump so that the filters are "sucked" tightly to the bottom and walls of the funnel.

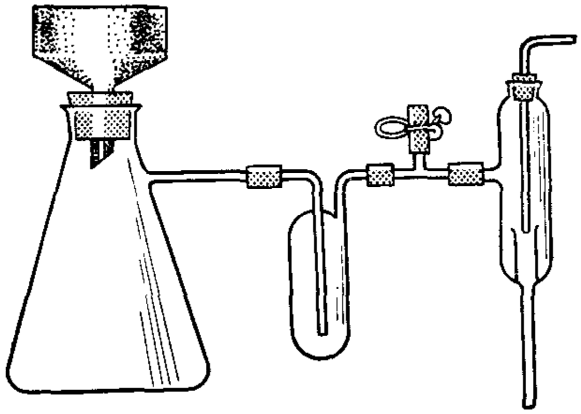


Fig. 19. Filtration under reduced pressure

Before beginning filtration, open the clamp of the tee and switch off the pump. Transfer the solution with the precipitate into the Büchner funnel along a glass rod, then close the clamp and switch on the water-jet pump. When the major part of the liquid has been filtered and the precipitate has become compact, see that there are no cracks in it. If cracks form on the surface of the precipitate, carefully smooth them out with a glass rod or the wide part of a glass stopper.

For the more complete separation of the filtrate from the precipitate, press the latter slightly against the funnel bottom with a glass stopper. Filtration is considered to be complete if filtrate drops no longer appear at the tip of the funnel. Prior to closing the cock of the water-jet pump, "extinguish" the vacuum in the suction flask. To do this, open the safety clamp on the outlet tube or extract the stopper with the funnel from the suction flask.

To remove the precipitate from the Büchner funnel, turn it over onto a sheet of filter paper on glass. When you slightly tap the funnel, the precipitate will fall onto the paper.

Funnels or crucibles with a soldered in porous or sintered glass plate have found wide application in laboratory practice. These plates are characterized by a diverse pore size, which is designated by the relevant filter number:

Number of sintered glass crucible	1	2	3	4
Average pore size, μm	120-100	50-40	30-20	10-5

Such filters are stable with respect to inorganic and organic acids except for hydrofluoric acid, and are quite stable to the action of alkalies in the cold.

Crucibles No. 1 and 2 are used for separating coarse-grain precipitates, and No. 3 and 4 for separating fine-grain ones. Sintered glass funnels and crucibles are put instead of a Büchner funnel into a suction flask with connection to a water-jet pump.

Centrifuging is employed for washing and separating jelly-like precipitates (hydroxides, sulphides). The precipitation of solid phase particles is accelerated under the effect of the centrifugal force developed in the rapid rotation of a centrifuge.

When using an electrical centrifuge, see without fail that tubes with solutions placed in opposite holders have the same mass. After switching on the centrifuge, control its speed in accordance with the instructions for the given centrifuge type. At the end of centrifuging, place the handle of the speed governor in its "zero" position. When rotation has stopped, switch off the centrifuge from the current source, open the centrifuge lid, and extract the tubes. Decant the liquid, and if the precipitate has to be washed, repeat the centrifuging after pouring the relevant washing liquid (water, alcohol, etc.) into the tubes and stirring their contents.

WORK WITH LABORATORY WARE ON GROUND JOINTS

In laboratory practice, it is very convenient to use ware and connecting tubes with ground joints. This enables one to obtain a tight (hermetic) connection of individual parts of a setup that can be easily disconnected if required. Standard taper joints are preferred whose dimensions are established by the relevant standards. The basic quantity in designating joints is the maximum diameter of the ground zone (mm). The length of this zone is also indicated (mm). The most widespread (in manufacturing ware and stoppers) are standard joints with the following ratios of the diameter and length of the ground zone: 14, 5/23, 19/26, 29/32 and 45/40.

Ground joints, like glass cocks, must never be used without lubrication! They are easily damaged if this is done, and the tightness of the connection will be disturbed. Clean the surface of a joint before applying a lubricant to it. Choose the latter depending on the process to be carried out in the ware with joints.

Use a special vacuum grease for work with a vacuum. Apply it to a joint after thoroughly washing the latter in an organic solvent (ether, acetone, carbon tetrachloride, etc.). Use a very small amount of the grease when lubricating a joint. Abundantly lubricated joints and cocks may leak. Apply the grease with your finger or with a a small horn or metal spatula uniformly over a zone about several millimetres wide in the broad internal part of the joint. Next slightly heat both parts of the joint by the luminous flame of a burner, connect them, and carefully turn them about their axis. Since vacuum grease

becomes very viscous with time, it is wise to change it completely before each experiment.

When working with aggressive gases or volatile liquids, use syrupy substances for lubrication, for instance phosphoric acid or concentrated sulphuric acid. However, owing to its lower viscosity and strong hygroscopicity, the latter is less suitable for this purpose.

Vaseline oil or glycerin is very often used for lubricating joints and cocks when working with non-aggressive compounds under conditions of room temperature.

DRYING OF SOLIDS

Crystalline and amorphous substances that are stable in the air and do not decompose when heated in the temperature interval from 100 to 130 °C are dried in a drying cabinet. The same substances can be dried in the air and in a desiccator over phosphorus anhydride, anhydrous calcium chloride, or concentrated sulphuric acid.

Dry substances containing water of crystallization in desiccators over a drying agent and see that the water vapour pressure over it (Table 2) corresponds to the water vapour pressure over the crystallohydrate being dried.

Table 2. WATER VAPOUR PRESSURE OVER DRYING AGENTS

Substance	Water vapour pressure, mmHg (20 °C)	Substance	Water vapour pressure, mmHg (20 °C)
Copper sulphate	1.4	Potassium hydroxide	0.002
Calcium chloride	0.36	Magnesium perchlorate	0.000 5
Sodium hydroxide	0.16	Phosphorus(V) oxide	0.000 02
Sulphuric acid (conc.)	0.003		

Dry hygroscopic solids containing no water of crystallization in a desiccator over a drying agent. Dry solids that are easily hydrolyzed by the moisture of the air, and also substances oxidized by the oxygen of the air in a vacuum desiccator or in a special vacuum drying cabinet. The vacuum in such cabinets is produced by an oil pump.

A vacuum desiccator has a side arm with a cock by means of which it is connected via a protective wash bottle to a water-jet pump producing a vacuum in the desiccator.

DRYING OF ORGANIC SOLVENTS

In preparative inorganic chemistry, synthesis in an organic solvent is used quite widely, especially when preparing inorganic substances that greatly hydrolyze. The organic substances used for this purpose, which are thoroughly dried, must not contain even traces of moisture. Below are given the procedures followed in drying

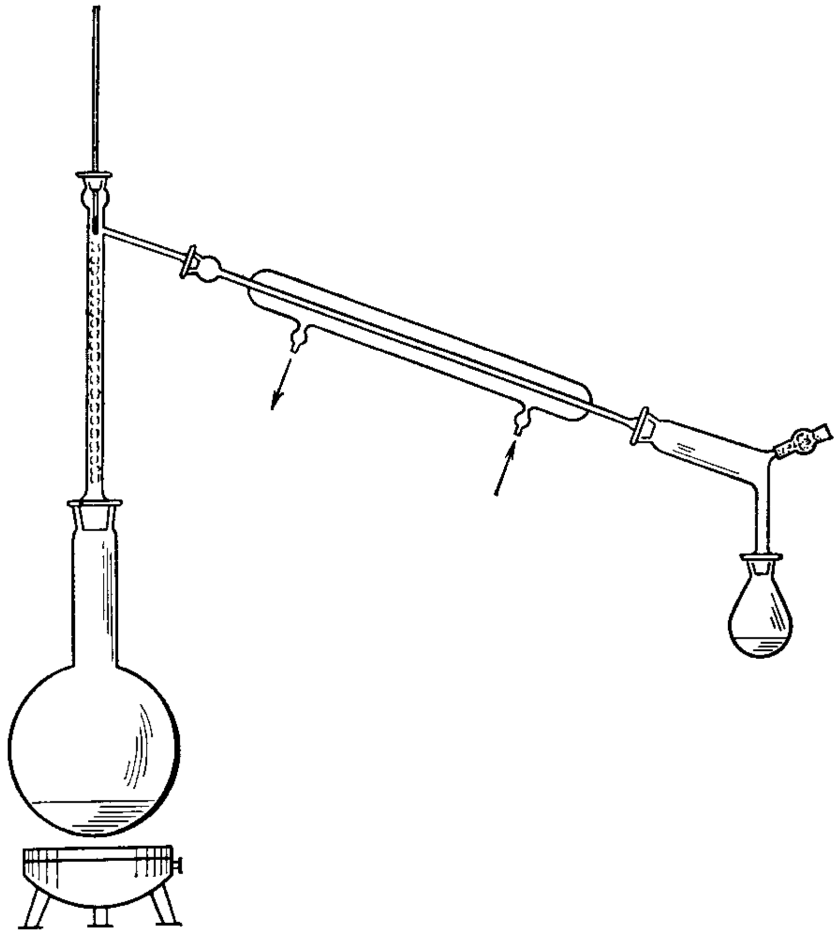


Fig. 20. Apparatus for distilling liquids

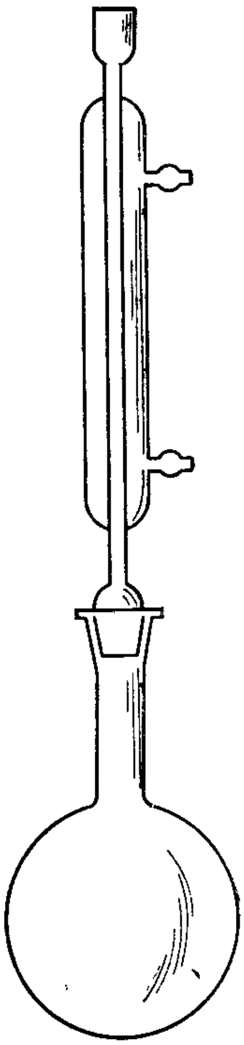


Fig. 21. Apparatus for heating liquids with a reflux condenser

the organic solvents used the most frequently in laboratories. Find their boiling points in a reference book.

Diethyl Ether. *Drying with a zeolite.* Put 500 ml of diethyl ether and 50-100 g of freshly roasted zeolite of Grade NaA or CaX into a one-litre flask provided with a stopper and a calcium chloride tube filled with roasted calcium chloride. The water capacity of the zeolite and its roasting temperature are indicated on the label. It is recommended to hold the ether over the zeolite about two days.

Drying with Phosphorus(V) Oxide. If no zeolite is available, phosphorus(V) oxide may be used. Put 500 ml of diethyl ether and 50 g of phosphorus(V) oxide into a one-litre flask provided with a stopper and a calcium chloride tube filled with calcium chloride. Mix the contents of the flask from time to time by carefully shaking it and let the mixture stand for two days. Then pour off the ether from the black oily liquid at the bottom of the flask and distil the ether over metallic sodium.

Distillation of Ether over Metallic Sodium. (*Do not distil the liquid to the end!*) Assemble the apparatus (Fig. 20). Put 5-10 g of metallic sodium dried with filter paper, cleaned of its oxide film, and cut up into pieces (about 5 × 5 mm in size) and 300 ml of ether into the flask. Connect a cooler with a receiver to the flask with the ether. *Heat the distillation flask on a water bath placed on an electric stove with an enclosed coil.* The distilled ether in contact with freshly cut lustrous metallic sodium should produce a faint cloud of hydrogen bubbles.

Store ether over metallic sodium in a bottle with a cork stopper provided with a calcium chloride tube containing calcium chloride.

Methanol. Commercial methanol contains less than 0.3% of water and may be used for the experiments set out herein without additional drying. The water content in it can be controlled by measuring its density with a densimeter (Table 3).

Table 3. DENSITY OF SOLVENT DEPENDING ON ITS WATER CONTENT

Methanol		Ethanol	
density, g/ml	water content, %	density, g/ml	water content, %
0.7917	0	0.7893	0
0.7948	1	0.7924	1
0.7976	2	0.7955	2
0.8005	3	0.7985	3
0.8034	4	0.8014	4
0.8062	5	0.8042	5
0.8090	6	0.8070	6
0.8118	7	0.8098	7

Ethanol. Assemble an apparatus (Fig. 21). Pour 1 litre of ethanol into a 2-litre round-bottomed flask provided with a reflux condenser, add 150 g of Grade NaA or CaA zeolite or 200 g of freshly roasted calcium oxide and boil the ethanol during 24 hours. Next replace the reflux condenser with an inclined one (see Fig. 20) and distil off the

ethanol. Measure the density of the distilled ethanol. Use Table 3 to determine its water content.

Carbon Tetrachloride. Put 30-40 g of anhydrous calcium chloride into the flask of an apparatus for distilling liquids (see Fig. 20) and pour in 0.5 litre of carbon tetrachloride. Hold the carbon tetrachloride over the drying agent for one day, then distil it off into a dry receiver.

BALANCES AND WEIGHING

Weighing with various accuracy is required in laboratory practice. A technical chemical balance is used for weighing with an accuracy up to 0.01 g. A conventional analytical balance (Fig. 22*a*) can be used for weighing with an accuracy up to 0.000 2 g.

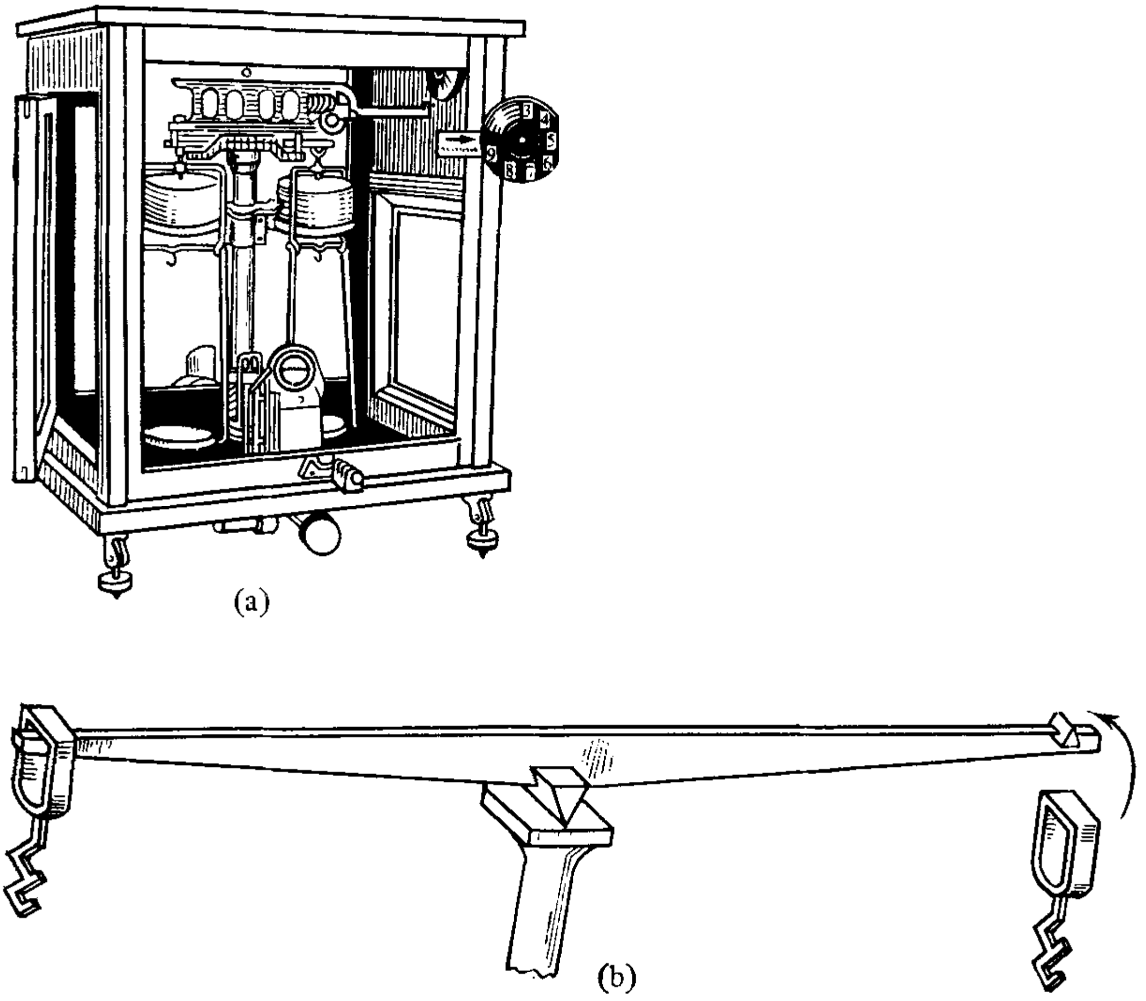


Fig. 22. An analytical balance

Balances of both kinds can be equal-arm or single-pan ones.

Balance Design. The principle underlying the design of technical chemical and analytical equal-arm balances is the same. A metal beam (equal-arm lever) is provided with three knife edges—two at its ends and one at its middle (Fig. 22*b*).

The middle knife edge rests on a plate on the central column of the balance and is the point of support. In an analytical balance, the knife edges and plate are made from agate or synthetic sapphire. The stirrups carrying the balance pans rest on the side knife edges. The beam is provided with a long pointer that indicates the deviation of the beam from a horizontal position on a scale. When the beam is horizontal, the pointer is opposite zero of the scale.

When a balance is not being used, all its moving parts should be lifted and the knife edges separated from their bearing surfaces by means of a device called an arrester. In this position of the balance, the beam cannot rock. This prevents excessive wear of the knife edges.

The beam is the sensitive element of a balance because its position is determined by the load at both sides of the central knife edge. Some balances are outfitted with a special device called a damper. The latter shortens the time needed for the beam to come to rest in a stable state of equilibrium. Such a balance is called damped.

An analytical balance is accommodated in a glazed cabinet whose front wall can be raised and whose side doors can be opened. The cabinet protects the balance from dust and air streams. The latter make accurate weighing impossible. The substance to be weighed and the weights are placed on the balance pans when the doors are open; the front wall is lifted only for repairs of the balance. During weighing, and also when the balance is not being used, all the doors must be shut. An analytical balance is provided with a set of different weights having a mass of 50, 20, 10, 5, 2, 1 grammes and 500, 200, 100, 50, 20, 10 milligrammes.

Larger weights are also used for weighing on technical chemical balances. The weights are kept in a box in a definite order that must be strictly observed. The "lugs" of the milligramme weights should be turned to the right.

Weighing Rules. Prior to weighing, see that the balance is in good order. Turn the arrester handle clockwise and watch the rocking of the pointer. If the pointer deviates from zero by the same number of graduations to the left and right, or the deviations in one direction differ by at most 1-1.5 graduations from those in the other one, consider that the balance is in good order. After checking the zero point, close the arrester. If the pointer does not deviate from zero as indicated above, inform your instructor that the balance is not in good order.

Put the substance to be weighed on a dry glass plate, in a weighing bottle or glass whose weight has been determined beforehand. When weighing a liquid, see that no drops of it get onto the balance pan. The substance being weighed must have the same temperature as that of the balance.

Place the object to be weighed on the left pan of the balance, and

the weights on the right pan. Put the box with weights on the table near the balance at the right side. Handle the weights only with pincers and in a definite sequence. Begin with the greater weight and then add the following ones as required with a constantly decreasing mass*. Put weights or loads on the balance pans and remove them only when the balance is arrested.

Weighing on a technical chemical balance may be considered completed when the addition of a 0.01-gramme weight is insufficient, and of a 0.02-gramme weight is excessive.

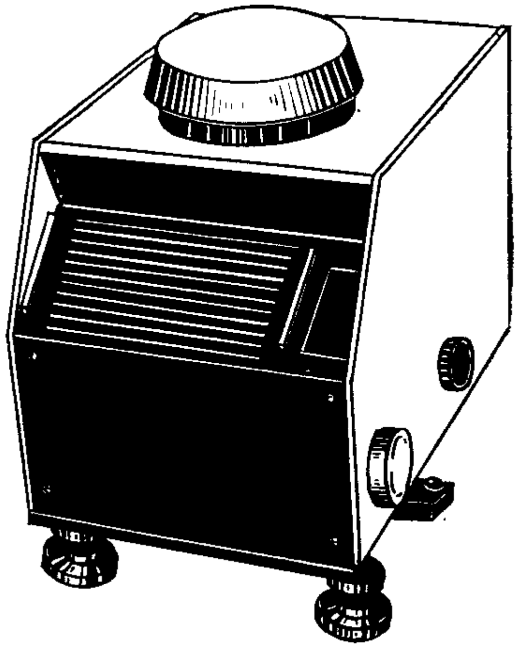


Fig. 23. A single-pan balance

On an analytical damped balance (see Fig. 22), tenths and hundredths of a gramme are loaded with the aid of a special mechanism manipulated by means of disks at the right-hand side of the front balance wall. Thousandths and ten thousandths of a gramme are indicated by the position of the pointer on an illuminated scale in the lower part of the balance between its pans.

After weighing, write the found weight in your notebook and put the weights in the required order into the nests of the box. When doing this, check your entry in the notebook. Never use a balance to weigh a load exceeding its maximum capacity.

A single-pan balance (Fig. 23) is intended for rapid weighing without the use of weights. The balance is designed for weighing loads with a mass from 0 to 200 g.

A single-pan balance designed for rapid weighing has no arrester, therefore take great care when placing a load on the pan. For weighing, first switch on the balance illumination with the aid of the tumbler switch on the rear panel of the balance body, and next set the indicator at zero by using the knob on the right-hand side of the balance. The knob is usually coloured differently than the balance body. Put the substance to be weighed in a glass or porcelain container of known weight and then carefully place the latter on the balance pan. Write down the reading that appears on the illuminated scale. The numbers on the scale indicate grammes, and one division of the scale corresponds to 0.1 g. The accuracy of weighing within the

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* For a detailed description of the rules for weighing on an analytical balance, see a guide on weight analysis.

interval of 5-200 g is 0.1 g. To see that the balance operates with satisfactory accuracy within the interval of 0-5 g, calibrate the scale with the aid of weights.

WORK WITH GLASS

Everyone working in a chemical laboratory must be able to perform the simplest glass shaping operations, namely, cutting glass rods and tubes, fusing them, bending tubes, and drawing capillaries.

Glass Cutting. Glass tubes and rods are cut with a hard steel knife or file. To cut off a length of tubing, make a mark with a file at the required spot. Next, while holding the tube in your left hand or having placed it on a table, file a notch at the marked place, pressing slightly on the file. After this, break the tube. To do this, hold it with both hands with your thumbs at opposite sides of the notch, slightly bend the tube ends toward yourself and simultaneously stretch the tube somewhat.

Tubes up to 10-12 mm in diameter can be cut in this way. When properly notched, a tube breaks easily, forming clean edges without burrs. To cut wider tubes, tie a thick thread wetted with ethonol around the notched spot. Ignite the thread, and the glass at this spot will crack smoothly.

Fusing of Glass. When using a cut off tube or rod with a sharp edge, you may cut your hand or spoil a cork or rubber stopper which you are fitting onto such a tube. To smooth a sharp glass edge, it must be fused. To do this, heat the tube end in the upper part of a flame and constantly rotate the tube about its axis until the glass softens somewhat, which is indicated by the yellow colour of the flame, and begins to melt. Remove the tube (or rod) from the flame and let it gradually cool.

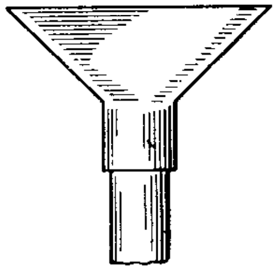


Fig. 24. A special "dovetail" nozzle for a gas burner

Tube Bending. To bend a glass tube, heat a part of it about five or six centimetres long on a wide flat flame. You can obtain such a flame by fitting a special nozzle ("dovetail") (Fig. 24) onto a gas burner. Hold the tube in both hands and heat the part to be bent in the upper part of the flame while continuously rotating the tube in one direction. When the glass softens and the tube begins to bend by itself, remove it from the flame and bend it quickly by smoothly urging its ends upward. A properly bent tube (Fig. 25*a*) should have no folds and constrictions (Fig. 25*b*).

Drawing out a Tube End and Making Capillaries. To draw out the end of a tube (Fig. 25*c*) or a capillary (Fig. 25*d*), heat the tube

until it softens, extract it from the flame and slowly draw it out to the required diameter. When the tube has cooled, carefully notch it and break off the superfluous tip.

Sealing of Tubes. To seal a tube, draw out its end and cut off the superfluous part. Next, while constantly rotating the tube, heat

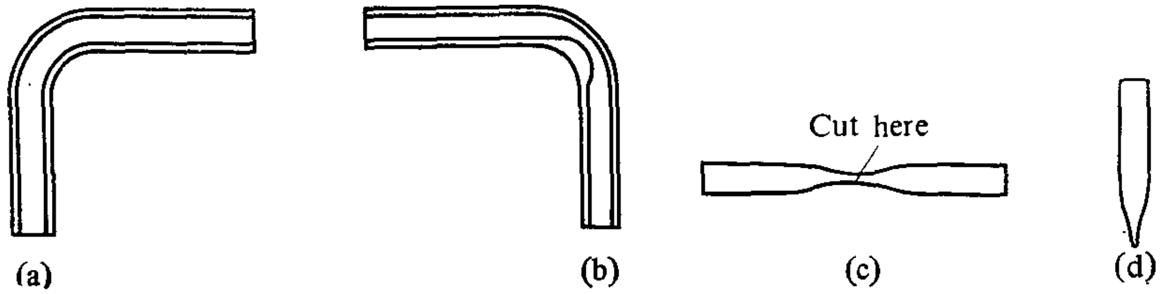


Fig. 25. Glass tubes: *a*—bent correctly; *b*—bent improperly; *c*—with drawn out end; *d*—with capillary cross section

its drawn out end in the upper part of a burner flame until the opening fuses and the tube end becomes round.

Usually a thickened sealed end is obtained, and it can easily crack. To avoid a thickened tube end, remove it from the flame after sealing and carefully blow air into the cold part of the tube until a properly rounded end is obtained.

STOPPERS

Choice of Stoppers. Cork and rubber stoppers are generally used in a laboratory. It is very important to choose a suitable stopper for a vessel. Take a cork stopper that enters the vessel opening with difficulty (i.e. is slightly larger than the opening) and compress it with a cork kneader, after which it becomes soft and fits well into the opening.

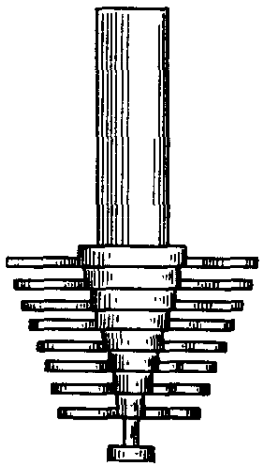


Fig. 26. A set of drill bits

Choose a rubber stopper for a vessel opening so that it fits into the latter more than half way. This is especially important when a glass tube will be inserted later into the stopper.

Never use cork or rubber stoppers to close vessels with concentrated acids or alkalies because the latter destroy such stoppers.

Drilling of Stoppers. Select a bit of the proper size (Fig. 26) for drilling a hole in a stopper. For a cork stopper, the bit diameter must

be somewhat smaller than that of the glass tube to be inserted into it. The bit diameter for a rubber stopper must correspond to the relevant tube diameter or be somewhat larger than it.

Take a cork stopper in your left hand and mark its narrow end with the bit where the hole is to be, next begin to revolve the drill by its handle in one direction while applying a slight pressure. See that the drill and stopper axes coincide, otherwise the hole will be skew. When the bit almost reaches the end of the stopper, put the latter on a bigger cork or similar material on the table and continue to revolve the drill until the bit emerges from the stopper.

When drilling a rubber stopper, you will find it prudent to wet the tip of the bit with glycerin or a dilute ammonia solution and drill on a table as indicated above, or in a special stopper drill (Fig. 27).

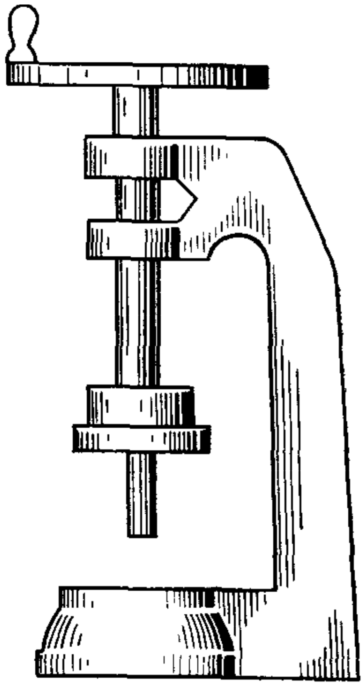


Fig. 27. A stopper drill

PRODUCING A VACUUM

It is often required in laboratory practice that the space in an apparatus should contain no air and other gases. Such a rarefied space is called a *vacuum*. Water-jet pumps produce a rarefaction of the order of several mmHg in a system, while modern vacuum equipment can produce a residual pressure ranging from 10^{-2} to 10^{-11} mmHg.

Water-jet pumps can be used wherever there is an adequate pressure of the water in the mains ($\geqslant$ 2 at or 196.2 kPa). The ultimate vacuum depends both on the design of the pump and the water temperature and cannot exceed the water vapour pressure at the given temperature (Appendix 1, Table 13).

At present, there are two basic techniques of producing a vacuum, namely, by means of vacuum pumps and by using special gas absorbers. A third auxiliary technique uses freezing out traps that lower the pressure of the vapour in a vacuum system.

The main parameters of vacuum pumps are:

1. The initial pressure from which normal operation of a pump begins.
2. The minimum pressure reached by the given pump, called the ultimate pressure. The ultimate vacuum is determined mainly by the vapour pressure of the working fluid.
3. The evacuation rate is determined not only by the evacuating

capacity of a pump, but also by the resistance of the connecting tubes to the flow. Therefore, to produce a high vacuum, never use too narrow delivery tubes and first of all narrow openings in cocks.

A vacuum up to 10^{-4} mmHg can be produced by a rotary (or mechanical) pump. Steam-jet pumps operate within the range from 10^{-2} to 10^{-7} mmHg. Gas absorbers are used to produce a vacuum below 10^{-8} mmHg. Their operation limits are 10^{-8} to 10^{-11} mmHg.

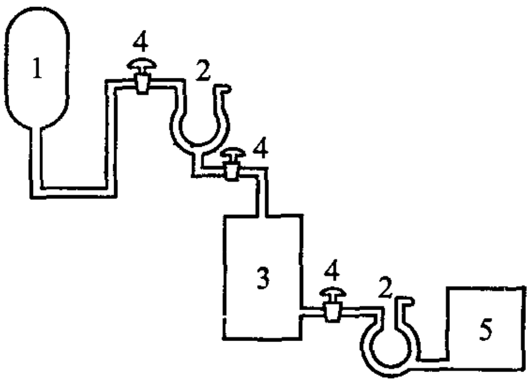


Fig. 28. A simplified vacuum setup: *1*—vessel being evacuated; *2*—cooled traps; *3*—steam-jet pump; *4*—vacuum valves; *5*—fore pump (pump for preliminary rarefaction)

Conventional setups generally consist of the following elements: (1) a fore pump (also called a primary or roughing pump) that produces and maintains the vacuum needed for the beginning of operation of the steam-jet pump. A mechanical pump is customarily employed for this purpose; (2) a steam-jet (oil or mercury) pump; (3) cooled traps, which assist the operation of the vacuum pumps by freezing water vapour and other gases condensing at a low temperature out of the system (the traps are cooled by liquid nitrogen); (4) a variety of valves and cocks required for controlling the setup; and (5) instruments for measuring the vacuum. Figure 28 shows a simplified diagram of a vacuum setup.

Mechanical Pumps. Most modern fore pumps are mechanical ones with a revolving rotor and oil seal. All pump models follow the same principle, although they differ in design.

The main part of all these pumps—an eccentric rotor—divides the internal pump space into several parts. This is achieved either by contact of the rotating eccentric with the stator surface (a valve pump) or by using movable vanes or plates. The latter may either be secured on the stator, being in sliding contact with the eccentric, (a stator-plate pump), or rotate together with the rotor, sliding over the internal surface of the stator (a rotary-plate pump, for example of the type shown in Fig. 29*a*).

Figure 29*b* shows schematically how a rotary-plate pump operates. The intake and discharge openings are indicated by arrows. The Roman numbers indicate the four characteristic positions of the rotor that it occupies consecutively during half a revolution. The direction of rotation is shown by an arrow. Let position *I* be the initial one. In position *II*, plate *A*, moving downward, produces a rarefaction at the intake opening side, into which the gas from the vacuum system flows. Plate *B*, moving upward, compresses the gas ahead of it and forces it out through the discharge opening. In posi-

tion *III*, plate *A* continues to suck in the gas, while plate *B* discharges the preceding portion of the compressed gas through the valve of the discharge opening. Position *IV* coincides with initial position *I*, the only difference being that the plates have exchanged places. Each plate thus plays a double role: on the one hand, it pulls along the gas flowing in through the intake opening from the vessel being evacuated, and on the other, it compresses the gas ahead of it sucked in by the other plate and discharges it out of the pump.

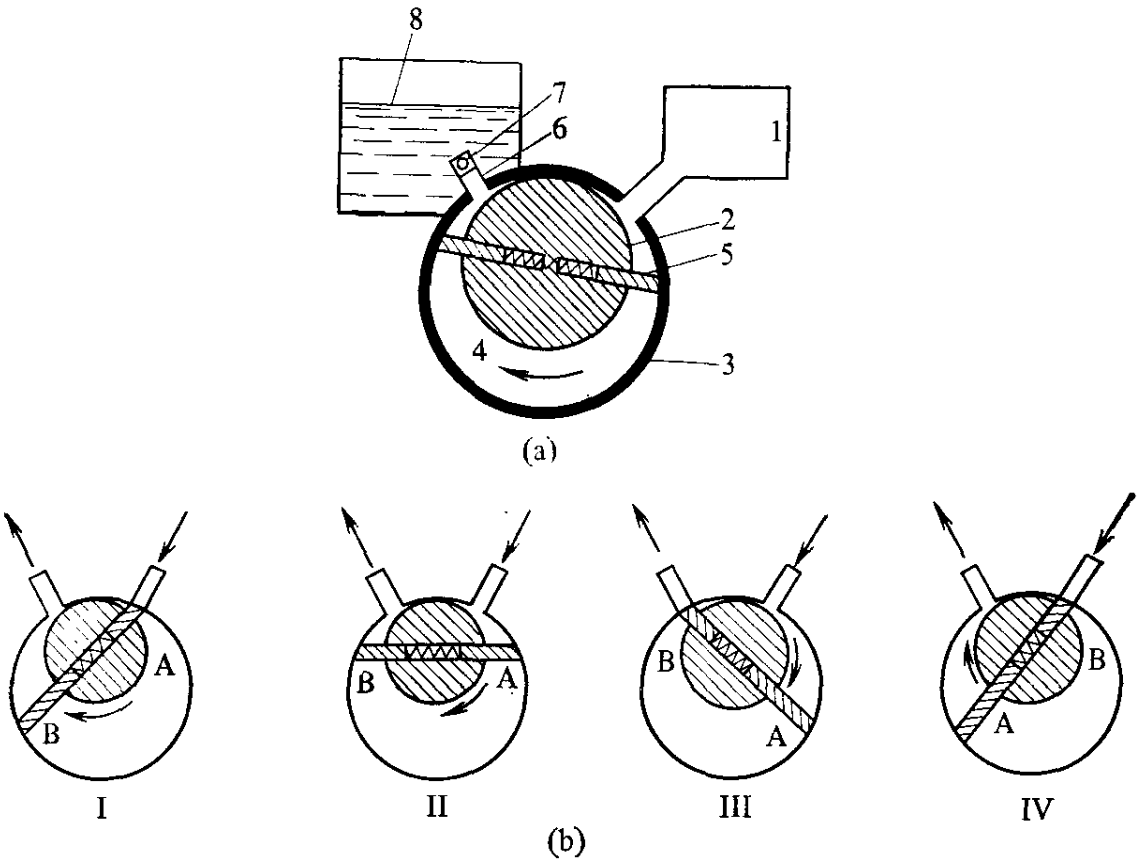


Fig. 29. A rotary-plate pump: *a*—schematic view; *b*—diagram of operation; *1*—system being evacuated; *2*—eccentric rotor; *3*—stator; *4*—space where gas is compressed; *5*—movable plates; *6*—discharge opening; *7*—discharge valve; *8*—oil seal over valve

During continuous rotation of the rotor, the gas is sucked in and discharged in turn by both plates, thus evacuating the system which the intake opening of the pump is connected to.

Oil contamination is one of the main causes of trouble in pumps. It increases the pressure of the oil vapour, which greatly lowers the ultimate vacuum. An increase in the oil vapour pressure is inevitable in an operating setup. An appreciable amount of water vapour is usually evacuated from the system so that the oil circulating in the pump forms an emulsion with the water retained in it. This leads to constant deterioration of the vacuum.

VACUUM MEASUREMENT

In vacuum engineering, one has to do with pressures ranging from 10^{-2} to 10^{-11} mmHg. It is impossible to measure such a broad range of pressures with a single vacuum gauge of a universal type. At present, a great variety of vacuum manometers and gauges is available. U-tube, thermal, and ionization manometers are used the most frequently in laboratory practice.

U-Tube Manometers. These are generally made from a glass tube bent in the shape of the letter U and partly filled with a working liquid, most often with mercury. The operation of the manometer is based on the displacement of the levels of the working liquid in both arms of the tube depending on the difference in the pressures over these levels. One arm of a manometer is connected to the vacuum setup in which the pressure is to be measured, while the other arm is either closed (soldered) or remains open, i.e. is constantly at atmospheric pressure.

Thermal Manometers. The principle of thermal manometer operation is based on the pressure dependence of the heat conductivity of a gas. This relation begins to manifest itself in the region of a moderate vacuum and gradually transforms into direct proportionality in the region of a high vacuum. At present, two types of thermal manometers, namely, the bridge and the thermocouple ones, predominate in laboratories.

A thermocouple manometer is a glass vessel with a tube for connection to a vacuum system. A heater is installed on two inlets to the vessel, while a thermocouple is welded to two other inlets. Its junction, in turn, is welded to the heater, to which a constant amount of heat is supplied. But since the heat conductivity of the residual gas in the system depends on the pressure, the withdrawal of heat from the heater is different at different pressures. Therefore, the temperature of the heater, which is measured by the thermocouple, also varies. The electromotive force (e.m.f.) produced will be proportional to the pressure. The millivoltmeter measuring the e.m.f. of the thermocouple is graduated in mmHg. Such a manometer can be used to measure a pressure from 10^{-1} to 10^{-3} mmHg.

Thermocouple manometers are used to measure the pressure in the tubing of a preliminary vacuum where no high accuracy is needed. These manometers are not damaged if the vacuum system gets under atmospheric pressure during their operation.

An **ionization manometer** is a glass vessel with a tube for connection to a vacuum system and three electrodes soldered into the vessel, namely, a cathode usually made from tungsten wire, a grid having a positive potential relative to the cathode and therefore being the anode, and an electrode with a negative potential relative to the cathode.

The electrons emitted by the heated cathode flow to the grid under the effect of the electric field and produce an electron current. The latter can be measured by an instrument included in the grid circuit.

If the grid potential is higher than the ionization potential of the residual gas, the gas in the manometer will become ionized when electrons collide with gas molecules. The positive ions formed in the course of ionization will flow to the negative electrode under the effect of the electric field of the latter. They give up their positive charge to this electrode and produce a current in its circuit that is measured by the relevant instrument. The negative electrode attracting positive ions is called an ion collector, while the current flowing in its circuit is called an ion current.

For a given gas, the current in the collector circuit is proportional to the concentration of the molecules in the region of pressures from 10^{-2} to 10^{-11} mmHg (consequently, the scale is of a linear nature).

In vacuum setups containing water, oil, or halogens, the cathode of the electronic valve is destroyed hopelessly after several hours of operation. To prevent this, ionization manometers are usually connected to a system of consecutively cooled traps.

APPARATUS ASSEMBLY

When performing laboratory work in inorganic synthesis, one has to assemble the required apparatus or setup from individual components, generally made of glass. The success of an experiment and also its safety often depend on the quality of apparatus assembly. This is especially important in the synthesis of readily hydrolyzing substances, and also in work performed in an atmosphere of hydrogen, carbon monoxide, or chlorine.

The main requirements which apparatuses assembled by students must meet is their good tightness, compactness, and an attractive appearance.

Remember that any assembled apparatus must have an outlet to the atmosphere (see, for example, Fig. 59*a*, p. 103).

The same apparatus can be used (when individual components, absorbents, or drying means are replaced) for synthesis of the most diverse compounds. Figure 61 (p. 105) shows an apparatus that can be used to produce chlorides, bromides, nitrides, sulphides, and hydrides of many metals. When the products are volatile, a special trap is installed at the end of the apparatus. When compounds that are unstable in moisture are being synthesized, a wash bottle or a column with a desiccant must be installed at the outlet from the apparatus.

When assembling an apparatus, remember that rubber tubes and stoppers can be affected by aggressive reagents (chlorine, bromine, etc.). To diminish this effect, and also to achieve compactness of the apparatus, use butt joints for gas outlet glass tubes with a minimum length of rubber tubes to connect them. When a butt joint of glass tubes in an apparatus is impossible (the tubes are at different heights) use an additional glass tube bent at the corresponding angle. Also remember that the volume of liquids contained in wash bottles must never exceed the volume of the inner tube of the bottle.

The edges of all glass tubes being used must be fused. Stoppers must enter the necks of flasks and the openings of reaction tubes about half way.

If an apparatus is provided with a thermometer (see Figs. 20 and 32), place it with the upper edge of the mercury bulb 0.5 cm below the discharge tube of the dephlegmator or Wurtz flask.

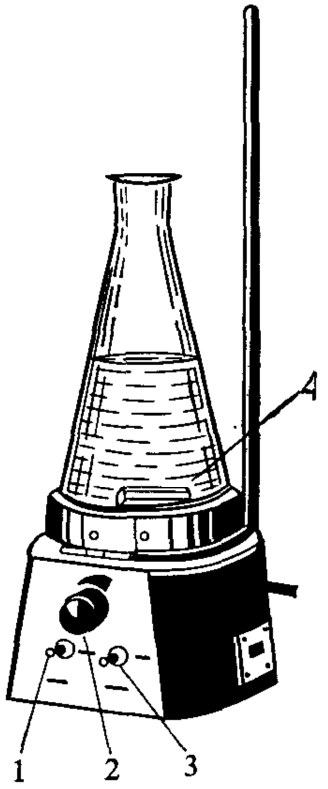


Fig. 30. A magnetic mixer

Mixing of Reactants. Reactants can be mixed manually with a glass rod (if the chemical reaction is being carried out in an open vessel), or by using mechanical or magnetic mixers.

A mechanical mixer consists of a glass rod with blades on its end. The rod is connected via a liquid seal to a motor powered from electric mains.

A magnetic mixer operates according to the principle of transmitting motion from a revolving rotor to the mixing rod by means of the magnetic field of the rotor (Fig. 30). The front wall of the mixer is provided with tumbler switch *1* for switching on the electric heater, knob *2* for controlling the magnetic rotor speed, and tumbler switch *3* for switching on the motor. The heater can function only when the motor is switched on. When knob *2* is turned clockwise, the speed of the rotor and, consequently, that of mixing rod *4*, grows. To prevent corrosion and chemical reaction with the substances being mixed, the rod is covered with a polyethylene coating or glass.

2 PURIFICATION OF SUBSTANCES

The most widespread purification techniques are recrystallization and sublimation for solids, filtration and distillation for liquids, and the separation of the impurities by absorbing them by various chemical reagents for gases.

2.1 SOLIDS

RECRYSTALLIZATION

Purification of Potassium Dichromate*. Using the table of solubilities (see Appendix 1, Table 1), calculate the amount of potassium dichromate that has to be taken to obtain a saturated solution in 50 ml of water at 60 °C.

Weigh the calculated amount of potassium dichromate on a technical chemical balance and triturate it in a mortar. Pour the powdered salt into a chemical beaker, and add 50 ml of water. Place the beaker on an asbestos gauze and heat with the flame of a gas burner almost to boiling while mixing the solution with a glass rod. Why is the solution heated almost to boiling and only then filtered?

To separate the insoluble impurities, filter the hot solution through a fluted filter into another beaker, using a funnel for hot filtration. While continuously stirring, cool the filtrate to room temperature, and then in a bath with ice to 0 °C.

Why does the intensity of the solution's colour change? Filter off the precipitated crystals through a Büchner funnel. What is contained in the mother solution?

Investigate the mother solution for the presence of a potassium sulphate impurity**. To do this, add one or two drops of concentrated hydrochloric acid and a solution of barium chloride to 2-3 ml of the mother solution diluted with 5-10 ml of distilled water. In a similar way, determine whether potassium sulphate is present in the separated solid potassium dichromate. Compare the results obtained. Transfer the potassium dichromate into a preliminarily weighed porcelain bowl and place it for 30-40 min into a drying cabinet (100 °C). After cooling, weigh the dichromate on a technical chemical balance.

Repeat the crystallization of the potassium dichromate (for what purpose?). Calculate the amount of water needed to obtain a potassi-

* One can purify potassium nitrate, potassium and sodium sulphates, aluminium potassium alum, and other salts in the same way.

** When recrystallizing sulphates, determine the presence of an impurity formed by a chloride ion.

um dichromate solution saturated at 60 °C. Is hot filtration obligatory during the repeated crystallization? Put the crystals obtained on a watch glass or into a porcelain bowl and dry them in a drying cabinet during one hour at 110-120 °C. After removing the bowl (or watch glass) with the preparation from the cabinet, put it into a desiccator (why?) for cooling, weigh it with an accuracy up to 0.1 g and return it to the drying cabinet for half an hour. Dry up to a constant weight. See whether the potassium dichromate obtained after the repeated crystallization contains a sulphate impurity. Determine the yield as a per cent of the initial mass of the specimen, and also the theoretically possible yield. What losses cannot be avoided in recrystallization?

Purification of Ammonium (Sodium, Potassium) Chloride. Prepare a saturated solution of ammonium chloride at 60 °C, taking 50 ml of water and the calculated amount of salt for this purpose. Heat the solution almost to boiling, filter it through a funnel for hot filtration, pour the filtrate into a porcelain bowl, put it on a water bath, and evaporate it up to half of the initial volume. Why is it necessary to remove part of the water by evaporation in this experiment?

Transfer the contents of the bowl into a beaker and cool it in a bath with ice. Filter out the precipitated crystals in a Büchner funnel, and dry them in the air. Calculate the yield in per cent. Why should ammonium chloride be dried in the air, and not in a drying cabinet? How should sodium and potassium chlorides be dried?

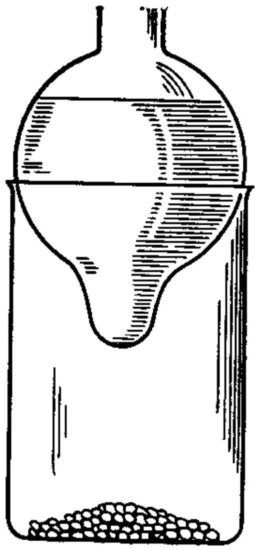


Fig. 31. A setup for purifying iodine by sublimation

SUBLIMATION

Purification of Iodine. Put 0.5 g of crystalline iodine and 0.2 g of potassium iodide (why is the latter added?) on the bottom of a low beaker without a spout (Fig. 31). Insert a flask with a bulge in its bottom into the beaker. Fill the flask with cold water, preferably running. Place the setup on an asbestos gauze and carefully heat the bottom of the beaker with a gas burner. See that the water in the flask is cold during the experiment. What is observed? Gather the crystals of the sublimed iodine in a weighing bottle or on a watch glass and weigh them. Determine the yield of iodine in per cent.

2.2 PURIFICATION AND DISTILLATION OF LIQUIDS

Purification of Water from Substances Dissolved in It. Assemble an apparatus as shown in Fig. 32. Fill cooler *2* with water. Feed the water upward through the cooler (why?). Prepare (draw out) 8-10 glass capillaries 10-12 mm long and seal them at one end.

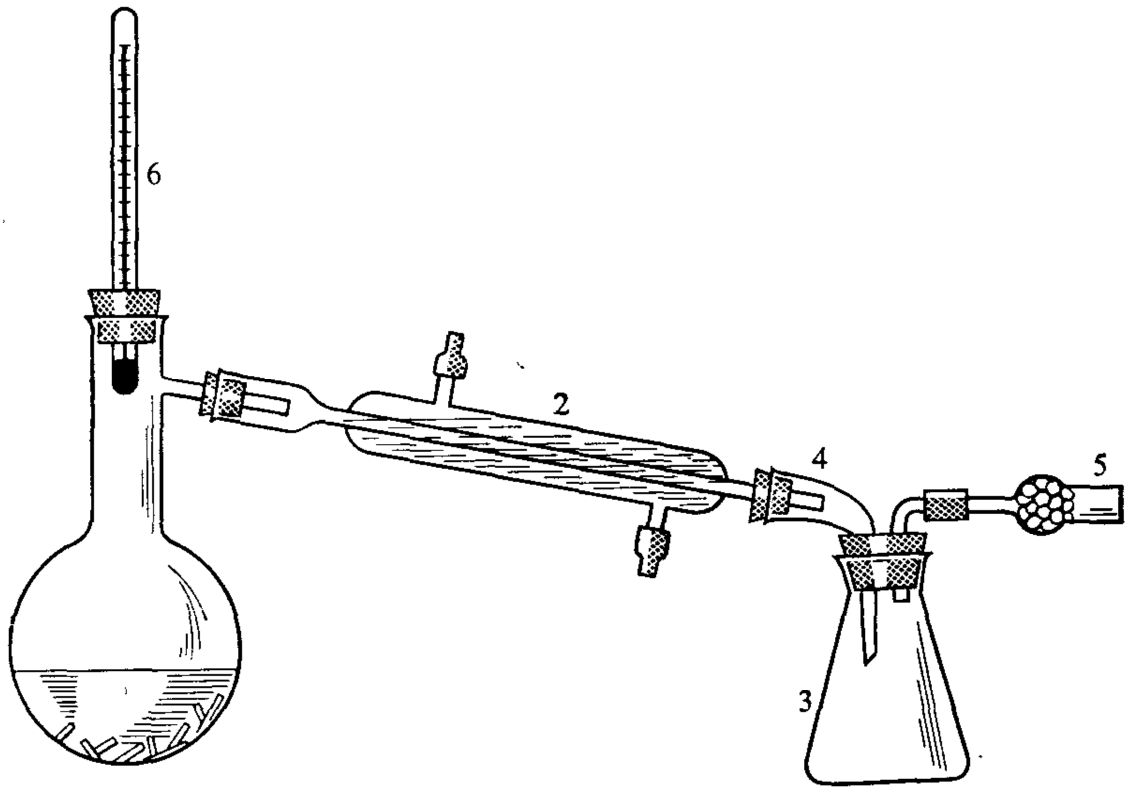


Fig. 32. An apparatus for purifying water from substances dissolved in it

Into Wurtz flask *1* with a capacity of 0.5 litre pour 250 ml of a potassium chloride or copper sulphate solution after having measured the density of the solution with a densimeter. Submerge the prepared glass capillaries in the flask containing the liquid with their open ends downward (why?). Close the opening of flask *1* with a stopper containing thermometer *6*. Heat the solution in the flask to boiling with a burner through an asbestos gauze. Note the temperature at which the solution boils. Stop heating flask *1* when 100-120 ml of liquid gather in receiver *3*. Disconnect the receiver from the apparatus. Measure the density of the distilled liquid. Does it contain potassium chloride (copper sulphate)?

Preparation of Hydrochloric Acid with an Azeotropic Composition (*perform the experiment in a fume cupboard*). Assemble an apparatus as shown in Fig. 20 with a few alterations. Take a conical or flat-bottomed flask without a stopper as the receiver. Fill the cooler with water. Feed the water upward through the cooler (why?). Prepare (draw out) 8-10 glass capillaries 10-12 mm long and seal them at one end. Measure the density of the initial hydrochloric acid

(about 15%) with a densimeter (*in the presence of your instructor*) and determine its concentration in per cent.

Pour 250 ml of hydrochloric acid into a 0.5-litre round-bottomed flask. Submerge the prepared glass capillaries in the flask containing the acid with their open ends downward. Close the flask with a stopper containing a dephlegmator and a thermometer. Heat the acid in the flask up to boiling. Cover the receiver with cotton wool or filter paper. Note the initial temperature at which the acid boils. How will the temperature at which the acid boils change as the liquid is distilled?

When the boiling point of the liquid becomes constant, change the receiver and distil 100 ml of the liquid into the new receiver. Measure the density of the liquids in the receiver and in the Wurtz flask. What is the hydrogen chloride percentage in them? Define an azeotropic mixture.

2.3 GASES

Carbon Dioxide. Acquaint yourself with the design of a Kipp gas generator (Fig. 33) and charge it for the preparation of carbon dioxide. Remove stopper with cock *1* and charge middle sphere *2* up to one-third of its volume with crushed marble. Close the opening of middle reservoir *2* with a stopper containing a gas-discharge tube and open cock *1*. Pour a 20% solution of hydrochloric acid into the upper sphere of funnel *3* so that it fills the lower part of the Kipp gas generator and covers part of the marble in middle reservoir *2*. After this close cock *1*. What is observed? Write the equation of the chemical reaction occurring in the Kipp gas generator. What impurities may the produced carbon dioxide contain?

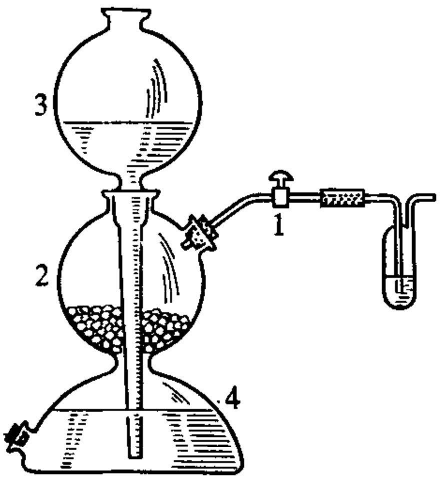


Fig. 33. A Kipp gas generator

Connect a wash bottle containing a large amount of distilled water to the Kipp gas generator and slowly pass carbon dioxide through it during 10-15 min. Analyse the contents of the wash bottle to see whether it contains hydrogen chloride. Remove the wash bottle. Connect a calcium chloride tube containing dehydrated copper sulphate to the Kipp gas generator. Pass a stream of carbon dioxide through it. Watch what happens. How can pure dry carbon dioxide be obtained?

2.4 SEPARATION AND PURIFICATION OF INORGANIC COMPOUNDS BY ION-EXCHANGE CHROMATOGRAPHY

Separating a Mixture of Cadmium and Copper Salts. Use a 50-ml burette as an ion-exchange column. At its lower end place a glass wool wad that will support a layer of resin (КУ-23 in the "hydrogen form") 30 cm high (see that the resin is constantly under a layer of water, even when it is being transferred from its jar). Also see that the column contains no air bubbles disturbing the monolithic nature of the layer and thus hindering the efficient separation of the mixture. Connect a 0.5-litre separatory funnel to the top of the burette using a rubber tube and a stopper for this purpose.

Prepare a mixture of 10 ml of a 0.5 *M* solution of cadmium nitrate and 10 ml of a 0.5 *M* solution of copper sulphate, dilute the mixture with water to 100 ml and thoroughly stir it. Transfer the mixture into the separatory funnel.

Pass the solution through the column at a rate of 5 ml/min, and then wash the column with 50 ml of hot water to remove the mineral acid. Check the completeness of absorption of the copper and cadmium ions. For this purpose, pour 3-5 ml of the washing water into a test tube and add a solution of ammonium sulphide or hydrogen-sulphide water to it. The formation of a precipitate indicates incomplete absorption, which occurs only if there is an error in performing the operations described above. In this case, the experiment has to be repeated. To do this, wash the column with a solution of hydrochloric acid (1 : 3), next with water until the washing solution has a neutral reaction, and then pass the solution through the column again.

To separate the cations, pass a solution of 5 ml of glycerin and 5 g of sodium hydroxide in 100 ml of water through the column at a rate of 5 ml/min. Gather the blue solution of copper glycerate at the outlet of the column. After the entire copper has been washed out of the column, rinse the resin with 50 ml of water, and then pass a 5% solution of hydrochloric acid through the column to wash out the cadmium in the form of the chloride. Check for the presence of cadmium in the solution by adding hydrogen-sulphide water or an ammonium sulphide solution to it.

Treat the copper glycerate and cadmium chloride solutions with a sodium sulphide solution up to the complete precipitation of the copper and cadmium sulphides. Filter the sulphide precipitates using a glass filter No. 4 and dry them at 100 °C. Weigh the dry substances and calculate their yield.

Separating a Mixture of Zinc and Iron Salts. Fill a column (see the preceding experiment) with КУ-2 resin in the "hydrogen form". Prepare a mixture of 10 ml of a 0.25 *M* zinc chloride solution and

10 ml of a 0.5 *M* iron(III) chloride solution. Pass the solution through the column at a rate of 1 ml/min, and then wash the resin with 20 ml of water. To extract the zinc cations, pass 250 ml of a 10% sodium hydroxide solution through the cation exchanger. Gather the sodium zincate solution flowing out from the column in a 300-ml flask.

Check for the complete extraction of the zinc cations from the cation exchanger. For this end, put a drop of the solution flowing out on a watch glass, add two drops of a 4 *M* solution of hydrochloric acid and one drop of a potassium hexacyanoferrate(II) solution. If zinc ions are present, a white precipitate of zinc hexacyanoferrate(II) forms. After extraction of the zinc, wash the resin with 20 ml of water. Dispose of the washing water.

To extract the iron(III) ions, pass 20 ml of a hot 2 *M* hydrochloric acid solution through the cation exchanger. Gather the solution flowing out from the column in a 250-ml flask. Use the reaction with potassium hexacyanoferrate(II) to check for the completeness of iron extraction.

Evaporate the sodium zincate solution to a volume of about 100 ml, and then add a sodium sulphide solution to it up to complete precipitation of the zinc sulphide. After settling, suck off the precipitate onto a glass filter and wash it with a small amount of water (10-15 ml). Dry the precipitate in a drying cabinet at 70-80 °C.

Transfer the iron(III) chloride solution into a porcelain bowl and evaporate it until crystallization begins. Cool the bowl with the crystals to 0 °C. Separate the crystals from the mother liquor using a glass filter No. 3. Weigh the obtained substances and calculate their yield.

2.5 SEPARATION AND PURIFICATION OF INORGANIC COMPOUNDS BY EXTRACTION

Separating a Mixture of Iron and Aluminium Salts. (*This experiment is a fire hazard! Perform all operations in a fume cupboard, in the presence of your instructor!*) Before separating the mixture, prepare a 36% aqueous solution of hydrochloric acid and an ether solution of this acid.

Assemble an apparatus for the preparation of hydrogen chloride (see Fig. 53, p. 91). Pass a stream of hydrogen chloride into a bottle containing concentrated hydrochloric acid cooled to 0 °C (constantly cool the bottle with ice) until the density of the acid becomes 1.19 g/cm^3.

To prepare an ether solution of hydrochloric acid, pour 150-200 ml of ether into a conical flask and cool the latter in a bath with dry ice. Without stopping the cooling, pass hydrogen chloride into the ether until there is no longer an odour of ether (about three hours).

Pour 25 ml each of 5% iron(III) chloride and aluminium chloride solutions into a 150-200-ml beaker. Add 25 ml of the 36% hydrochloric acid solution. Pour the solution into a 250-ml separatory funnel, add 50 ml of the ether saturated with hydrogen chloride, tightly close the funnel with a stopper and turn it over, holding the stopper with one hand and the cock with the other. With the funnel in this position, open the cock for a short time to level out the excess pressure arising because of evaporation of the ether. Next transfer the funnel to a horizontal position providing the maximum interface of the ether and water layer, and, while holding the cock and the stopper, shake the funnel, turning it upside down from time to time and opening the cock. Keep cooling the funnel with a stream of running water. After finishing the shaking, fasten the funnel in the clamp of a stand and let it stay there up to complete stratification of the liquid. Pour off the bottom layer into a flask. Pour the ether solution into a round-bottomed flask and close it with a glass stopper. Repeat the extraction from the aqueous layer, having added a new portion (50 ml) of ether saturated with hydrogen chloride. Combine the ether solutions obtained after the first and second extractions.

Pass a stream of air through the aqueous solution to remove the ether. Pour the solution into a porcelain bowl and evaporate it until crystallization begins. Add 50 ml of water to the flask with the ether solution, attach a cooler to the flask (see Fig. 20), and distil off the ether, *heating the flask with hot water.* Pass air through the remaining aqueous solution. As in the first case, transfer the solution into a porcelain bowl and evaporate it at 92-95 °C until crystallization begins. Cool the bowls to 0 or at least 4 °C. Separate the crystals formed from the mother liquor using a glass filter No. 3.

3 DETERMINATION OF MOLECULAR AND ATOMIC MASSES AND OF CHEMICAL EQUIVALENTS

3.1 MOLECULAR MASSES OF GASEOUS SUBSTANCES

Determining the Molecular Mass of Oxygen. Assemble a setup for determining the molecular mass of oxygen (Fig. 34) and check its tightness by parts.

Checking the Clamp. Fill the siphon with water. It must contain no air bubbles. To do this, take the test tube off stopper *1*, open clamp *3*, blow air through the tube with stopper *1*, and close the clamp again. See if any water flows out of the siphon tube.

Checking the Test Tube and the Setup as a Whole. Connect the test tube to the setup, lower the end of the tubing into the beaker with

water, open the clamp, turn the flask so that you can lower the beaker with water and thus free the end of the tubing. If the setup is tight, only a few drops of water may appear. Why?

Lower the end of the tubing into the beaker with water, close the clamp, and return the setup to its previous position. Fill flask *2* with water up to its neck (the volume of the flask should be one litre). Pour about 2 g of potassium chlorate into the refractory test tube of the setup so that no crystals remain in the upper part of the tube. Determine the mass of the test tube with the potassium chlorate approximately on a technical chemical balance, and then weigh it on an analytical balance with an accuracy up to 0.01 g. Carefully connect the test tube to the setup. Check the tightness of the latter again.

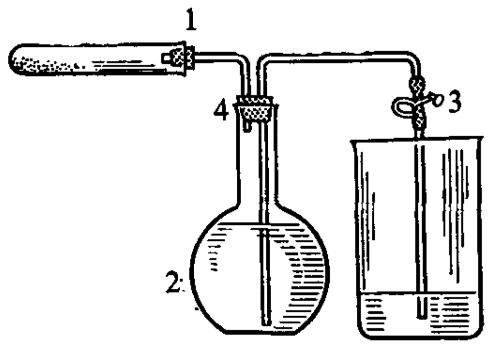


Fig. 34. A setup for determining the molecular mass of oxygen

Adjust the pressure in the flask to atmospheric. To do this, pour an amount of water into the beaker such that the surface of the water in both vessels will be at the same level when the clamp is open. Close the clamp and pour the water out of the beaker. Measure exactly 50 or 100 ml of water with a cylinder and pour it into the beaker, keeping the tip of the siphon submerged in the water. Open the clamp and without extracting the end of the tubing from the water, move the clamp onto stopper *4* to get it out of your way. (*Do this in the presence of your instructor.*)

First carefully heat the test tube using a small burner flame. Perform further heating so that the decomposition reaction is not too vigorous. Stop heating the test tube when 500-600 ml of water have passed into the beaker.

Let the setup cool to room temperature. Bring the pressure in it to atmospheric by lifting or lowering the beaker with water or the flask. Close the clamp. Measure the volume of the water in the beaker by pouring it into a measuring cylinder. Weigh the test tube on the analytical balance with the same accuracy as before.

Repeat the experiment (any quantitative determination must be repeated at least twice until similar results are obtained) as indicated above. Enter the results of your observations and calculations in your laboratory notebook, using Form 1.

Determining the Molecular Mass of Carbon Dioxide. Carbon dioxide can be prepared in a Kipp gas generator or taken from a cylinder in which it is stored under pressure. To determine the molecular mass of carbon dioxide, take a dry flat-bottomed 500-ml flask with a tightly fitting rubber stopper. Use a rubber band or a pencil for writing

Form 1. DETERMINATION OF MOLECULAR MASS OF OXYGEN

Item	Experiment No.	
	1	2
Mass of test tube with substance before heating, g		
Ditto, after heating, g		
Mass of evolved oxygen, g		
Atmospheric pressure (on barometer), mmHg		
Room temperature, °C		
Water vapour pressure, mmHg		
True pressure of oxygen in flask, mmHg		
Volume of water in beaker before experiment, ml		
Ditto, after experiment, ml		
Volume of evolved oxygen under conditions of experiment, ml		
Ditto, at standard temperature and pressure, ml		
Molecular mass of oxygen (calculate using the Mendeleev-Clapeyron equation and proceeding from the density of oxygen relative to air)		
Magnitude of error in determining molecular mass, %		

on glass to make a mark on the neck of the flask where the end of the stopper is. Weigh the flask with the stopper with an accuracy up to 0.01 g.

When filling the flask with carbon dioxide, lower the gas discharge tube of the Kipp gas generator or of the cylinder with carbon dioxide to the bottom of the flask. When the flask is filled with the carbon dioxide (how can this be determined?), slowly (why?) extract the gas discharge tube, close the flask opening with the stopper and

Form 2. DETERMINATION OF MOLECULAR MASS OF CARBON DIOXIDE

Item	Experiment No.	
	1	2
Mass of flask with carbon dioxide, g		
Ditto, with air, g		
Atmospheric pressure (on barometer), mmHg		
Temperature, °C		
Volume of air in flask under conditions of experiment, ml		
Ditto, at standard temperature and pressure, ml		
Mass of air in flask volume, g		
Mass of empty flask, g		
Mass of carbon dioxide in flask volume, g		
Mass of one litre of carbon dioxide, g (from data of experiment)		
Density of carbon dioxide relative to hydrogen		
Molecular mass of carbon dioxide		
Magnitude of error in determining molecular mass, %		

weigh it. Fill the flask with the carbon dioxide several times until a constant mass is obtained. Determine the volume of the flask by filling it with water up to the mark showing where the stopper ends and measuring the volume of the water. Record the temperature and pressure. Calculate the molecular mass of carbon dioxide. Enter your results in your laboratory notebook, using Form 2.

3.2 DETERMINATION OF MOLECULAR MASSES OF VOLATILE LIQUIDS FROM THEIR VAPOUR DENSITY

Determining the Molecular Mass of Ethyl Ether by Meyer's Method. (Ethanol can be used instead of ethyl ether.) To determine the vapour density of volatile liquids, a device is used (Fig. 35) consisting of glass vessel *1* whose bottom part is a cylinder with a volume of about 100 ml, while its upper part is a long narrow tube with two offtakes *2* and *4*. A glass rod reaching the opposite wall of the tube is inserted into offtake *2* via a rubber collar. The rod should be easily pulled back from the tube wall. Offtake *4* is connected to a long bent tube whose end is submerged in a bath with water. Eudiometer *6* filled with water and secured in the clamp of a stand (not shown in the figure) is submerged in the same bath. Vessel *1* is secured in a cork stopper in outer vessel *5* used for heating.

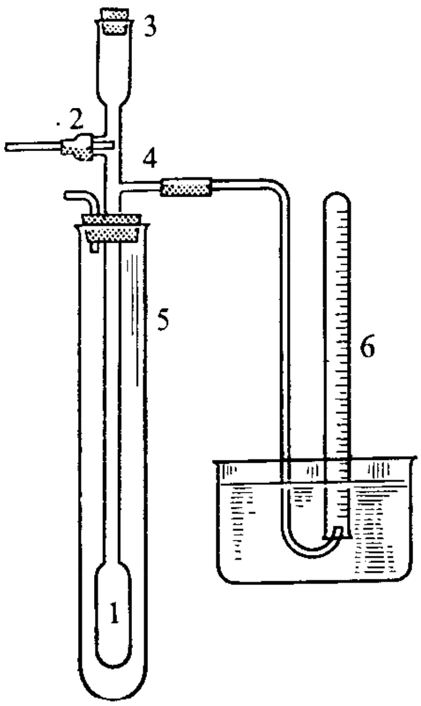


Fig. 35. A device for determining the vapour density of volatile liquids by Meyer's method

First of all, thoroughly dry vessel *1* with hot air. Pour 50-100 ml of water (if the boiling point of the liquid being studied is below that of water) into vessel *5*.

Next prepare ampoules. For this purpose, draw out a thin-walled glass tube 1·2 mm in diameter at both ends into capillaries 5-6 cm long. The volume of an ampoule must not exceed 0.1-0.15 ml. Determine the mass of an empty ampoule on an analytical balance. Slightly heat the wide part of the ampoule on a burner flame and immerse its tip into ether. When the ampoule is filled with ether, rapidly seal the capillaries at the tube ends on the small flame of

a burner. (*Seal an ampoule in the presence of your instructor, and wear eye protection!*)

Weigh the ampoule with the substance being tested. Open stopper *3* of the device and put the ampoule into the cylindrical vessel on the rod inserted into offtake *2*.

Heat the water in outer vessel *5* up to boiling. When the temperature of the air in vessel *1* reaches that of the boiling water (how can you determine this?), place the end of the gas discharge tube under the opening of eudiometer *6*, close stopper *3*, and, pulling back the glass rod in offtake *2*, drop the ampoule onto the bottom of the vessel, where it will break. When the evolution of bubbles stops, remove the gas discharge tube from the water and extinguish the burner. Bring the pressure of the air in the eudiometer to atmospheric. How can this be done? Calculate the molecular mass of the liquid being tested and enter the results in your laboratory notebook, using Form 3 for this purpose.

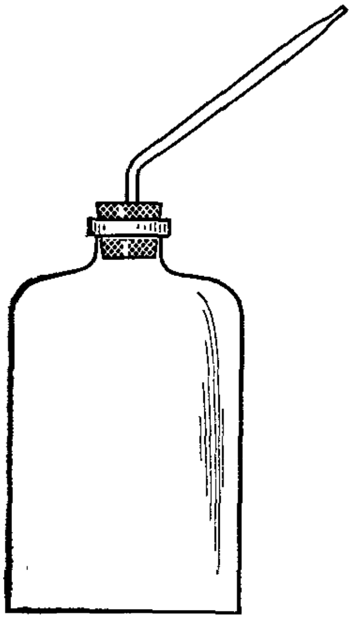


Fig. 36. A setup for determining the vapour density of volatile liquids by Dumas's method

Determining the Molecular Mass of Carbon Tetrachloride by Dumas's Method. Assemble the setup shown in Fig. 36. Bend a glass tube at an angle of 120° and draw out one end of it into a capillary. Insert the tube into the stopper closing the neck of a 100-ml bottle. Mark the neck of the bottle where the end of the stopper is. Weigh the bottle together with the rubber stopper and tube with an accuracy up to 0.01 g, measure 2-3 ml of carbon tetrachloride (acetone or ethanol can also be used) and transfer it into the bottle. Immerse the bottle up to its neck into a beaker with water having a copper gauze on its bottom. Heat the water in the beaker up to boiling and continue to heat it until all the liquid in the bottle has evaporated (about 10 min). Without removing the bottle from the beaker, seal the tip of the tube on the sharp flame of the burner. Record the room temperature, atmospheric pressure, and the boiling point of the water. Remove the bottle from the beaker, wipe it, and let it cool. Weigh the bottle with its contents and, submerging the bottle in water, remove the stopper under water. What happens?

Extract the bottle filled with water and close it with the stopper containing the tube also filled with water. Thoroughly wipe the entire setup and weigh it. Determine the mass of the water filling the

setup without taking into account the mass of the air in the volume of the setup. Enter the results in your laboratory notebook, using Form 4.

Form 3. DETERMINATION OF MOLECULAR MASS OF A VOLATILE LIQUID BY MEYER'S METHOD

Item	Experiment No.	
	1	2
Mass of ampoule, g		
Ditto, with liquid being tested, g		
Mass of liquid being tested, g		
Volume of displaced air, litre		
Atmospheric pressure, mmHg		
Temperature, °C		
Pressure of water vapour, mmHg		
Volume of vapour of liquid being tested at standard temperature and pressure, litre		
Molecular mass of liquid being tested		
Magnitude of error in determining molecular mass, %		

Form 4. DETERMINATION OF MOLECULAR MASS OF A VOLATILE LIQUID BY DUMAS'S METHOD

Item	Experiment No.	
	1	2
Mass of bottle with stopper, tube, and air, g		
Ditto, with stopper, tube, and condensate, g		
Ditto, with stopper, tube, and water, g		
Volume of bottle with tube at room temperature and atmospheric pressure, litre		
Temperature, °C		
Atmospheric pressure, mmHg		
Volume of air (liquid vapour) at standard temperature and pressure, litre		
Mass of air in volume of bottle, g		
Mass of empty bottle, g		
Mass of liquid vapour, g		
Vapour density relative to hydrogen		
Molecular mass of liquid		

3.3 DETERMINATION OF CHEMICAL EQUIVALENTS AND ATOMIC MASSES OF METALS

Determining the Equivalent of Magnesium. Assemble an apparatus as shown in Fig. 37. Take a flat-bottomed flask with a volume of one litre. Check the tightness of the apparatus. Weigh not over 0.5 g of a magnesium ribbon on an analytical balance with an accu-

racy up to 0.01 g. Calculate the volume of a 10% sulphuric acid solution that is needed to dissolve the taken amount of magnesium. Measure the required volume of the acid and add an excess of it in an amount of 100% by volume. Carefully pour the acid into a Wurtz flask without wetting the walls of its neck. Secure the flask in an inclined position in the clamp of the stand.

Place the weighed amount of the metal into the neck of the flask. Close the flask opening tightly with its stopper. Adjust the pressure

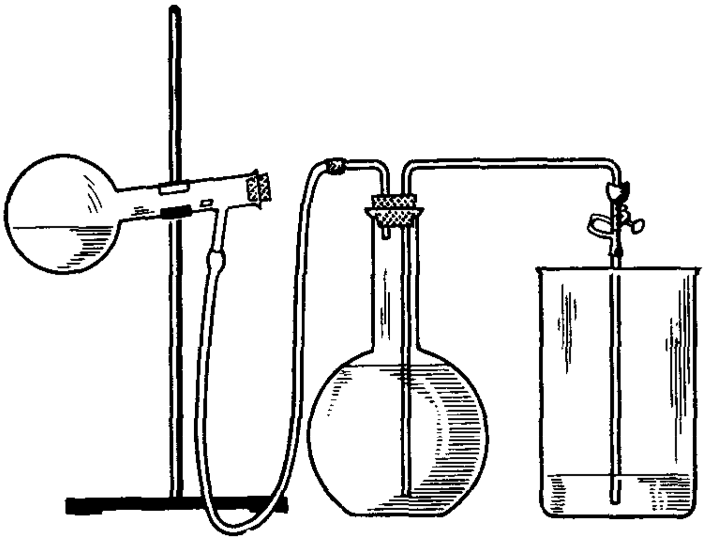


Fig. 37. An apparatus for determining the equivalents of metals

in the apparatus to atmospheric (see p. 54). Measure exactly 50 or 100 ml of water with a measuring glass and pour it into the beaker (the tip of the siphon must be submerged in the water). Open the clamp and move it along the connecting tube onto the stopper of the flask with water to get it out of your way. (*Do this in the presence of your instructor*). Turn the Wurtz flask to its vertical working position so that the metal drops into the acid. The flask gets heated as a result of the reaction.

After the apparatus has again reached room temperature, bring the pressure in it to atmospheric. Measure the volume of the water displaced from the apparatus by the evolved hydrogen. Write the equation of the chemical reaction. Calculate the equivalent of the metal taken. Compare the value of the found equivalent of magnesium with its true value, and enter the results in your laboratory notebook, using Form 5.

Determining the Equivalent of Zinc. (Determine the equivalent of zinc as in the preceding experiment.) Weigh about 1.3 g of granulated zinc on an analytical balance with an accuracy up to 0.01 g. Calculate the amount (by volume) of a 20% sulphuric acid solution that is needed for dissolving the zinc. Measure the calculated amount of acid with a measuring glass and add an excess of 100%. To acce-

Form 5. DETERMINATION OF THE EQUIVALENT OF A METAL (MAGNESIUM)

Item	Experiment No.	
	1	2
Mass of metal (magnesium), g		
Atmospheric pressure, mmHg		
Temperature, °C		
Water vapour pressure, mmHg *		
Volume of water in beaker before experiment, litre		
Ditto, after experiment, litre		
Volume of hydrogen under conditions of experiment, litre		
Ditto, at standard temperature and pressure, litre		
Equivalent of metal, g		
Magnitude of error in determining the equivalent, %		

* For the water vapour pressure, see Appendix 1, Table 13.

lerate the dissolution of the zinc, introduce a small piece of copper wire or pour one or two drops of a copper sulphate solution into the flask (for what purpose?).

Calculate the equivalent of zinc. Determine the magnitude of the error in computing it in per cent. Enter the results of your calculations and observations into your laboratory notebook as in the preceding experiment, using Form 5. Proceeding from the known valence of magnesium and zinc and your results, calculate the atomic masses of these elements. Compare the values obtained with tabulated data.

DETERMINATION OF THE ATOMIC MASS OF LEAD

(This experiment is performed by two students)

1. Determining the Approximate Value of the Atomic Mass of Lead from Its Specific Heat Capacity. To determine the specific heat capacity of a metal, use a calorimeter and a device for heating the metal. A very simple calorimeter can be made from several beakers inserted one into another (Fig. 38). The inner beaker should have a volume of 100 ml, the middle one—300-400 ml, and the outer one—500 ml. Water is poured into the small beaker, while the others are needed to produce an air thermal-insulating layer.

A device for heating a metal also consists of three beakers of different volumes inserted one into another so that the bottom of one beaker does not contact that of its neighbour. Unlike a calorimeter, water is poured into all three beakers.

Pour 50 ml of water into the small beaker of the heating device and an amount of it into the other two beakers such that the level

of the water in an outer beaker will be higher than in its inner neighbour. Take a piece of lead with a mass of 110-150 g and clean its surface with emery paper. Weigh the metal with an accuracy up to 0.1 g. Fasten the metal with a strong thread on a glass rod and immerse it in a beaker with water so that the metal touches neither the bottom nor the walls of the beaker. Put the heating device on a tripod with a gauze. Heat the water up to boiling with a gas burner. Keep the metal in the boiling water for 10-15 min (why?).

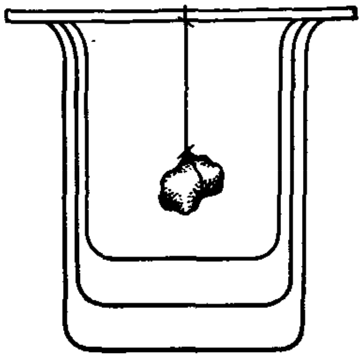


Fig. 38. A device for determining the atomic mass of a metal from its specific heat capacity

Weigh the small beaker of the calorimeter and pour exactly 50 ml of water into it. Measure and record the temperature of the boiling water in the heating device; this will be the temperature of the metal. Use another thermometer to measure the temperature of the water in the calorimeter.

Place the calorimeter next to the heating device and transfer the heated metal into the calorimeter beaker as rapidly as possible. Move the heating device away from the calorimeter and immediately begin to observe the change in the temperature while continuously stirring the water. Measure the temperature of the water every 10 seconds until it reaches a maximum and then begins to drop. Repeat the experiment, pouring 45 ml of water into the calorimeter. Enter the obtained results in your laboratory notebook, using Form 6.

Form 6. DETERMINATION OF THE ATOMIC MASS OF LEAD FROM ITS SPECIFIC HEAT CAPACITY

Item	Experiment No.	
	1	2
Mass of metal, g		
Temperature of metal, °C		
Volume of water in calorimeter, litre		
Initial temperature in calorimeter, °C		
Maximum temperature of water in calorimeter, °C		
Increase in temperature of water in calorimeter, K		
Decrease in temperature of metal, K		
Specific heat capacity of water, cal/g · K		
Ditto, of glass (from tabulated data), cal/g · K		
Amount of heat absorbed by glass of beaker and thermometer, cal		
Specific heat capacity of metal, cal/g · K		

To determine the amount of heat absorbed by the glass of the calorimeter beaker, mark the level of the water in the beaker when running the experiment. Use the data obtained to approximately determine the mass of the glass heated by the water. Consider that the mass of the thermometer glass immersed in the liquid is about 2 g. Use the found specific heat capacity to calculate the atomic mass of lead by the Dulong and Petit law.

2. Determining the Equivalent of Lead. Roast a clean porcelain bowl in a muffle furnace at 400-450 °C, and after cooling it in a desiccator, weigh it with an accuracy up to 0.01 g. Put about 0.5 g of granulated lead in the bowl and weigh it with the same accuracy. Pour 10 ml of a 40% nitric acid solution onto the metal, cover the bowl with a watch glass, and place it in a water bath. See what happens. Write the equation of the reaction.

When all the metal dissolves, carefully remove the watch glass, hold it above the porcelain bowl, wash off it the drops of the solution that might have gotten onto it when the metal was dissolved. Use a stream of water from a wash bottle for this purpose. Add 5 ml of concentrated hydrochloric acid to the bowl. What substance will precipitate?

Put the bowl with the solution and the precipitate in the water bath again, place a glass triangle on the bowl, and a watch glass on the triangle. Heat the bowl until a dry precipitate remains on its bottom. Carefully wash the watch glass and glass triangle with water from a wash bottle so that the washing water will be gathered in the bowl. Again add 3 ml of concentrated hydrochloric acid and evaporate the contents of the bowl until it is dry.

Transfer the bowl into a muffle furnace and roast the precipitate at 400-450 °C during one hour. Cool the bowl with the substance to room temperature in a desiccator and weigh it. Use the found value of the equivalent and the approximate value of the atomic mass of lead to determine its valence. Calculate a more accurate value of the atomic mass of lead from the obtained data, compare your result with the value of the atomic mass of this element given in Mendeleev's periodic table, and establish the magnitude of the error in per cent.

4 OXYGEN

Indicate the position of oxygen in Mendeleev's periodic table of the elements, the size of its atom, the electron configurations of the atom and molecule, and its oxidation states. How can the paramagnetic properties of liquid oxygen be explained?

4.1 PREPARATION

Work with a Gas Meter. Glass or metallic gas meters are used for gathering and storing gases. Gases moderately soluble in water, including oxygen, are gathered and stored in such meters over water.

A glass gas meter (Fig. 39*a*) consists of two parts, namely, funnel *1* provided with cock *2*, and thick-walled bottle *3* with opening *4*

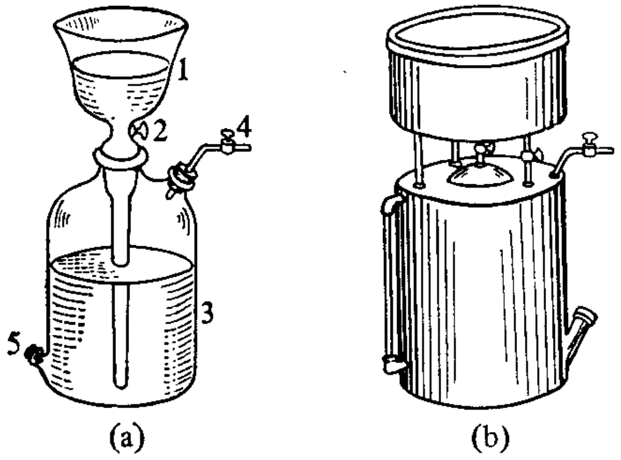


Fig. 39. Gas meters

for discharging the gas and opening *5* at the bottom for draining off the water.

Filling the Gas Meter with Water. Remove funnel *1* and fill bottle *3* with water. Invert funnel *1*, close cock *2*, fill the funnel tube with water, return the funnel to its initial position while closing the opening of its stem with your thumb. Rapidly submerge the funnel into bottle *3* filled up to its top with water. If air bubbles remain in the gas meter, remove them through cock *2* using a metal wire or by slightly rocking the gas meter.

Put the gas meter filled with water on the edge of a table near a sink. After closing all the cocks of the gas meter, open its bottom opening *5*. Does water flow out of the meter? (A metallic gas meter is shown in Fig. 39*b*).

Filling the Gas Meter with Oxygen. Measure the volume of the meter. Write the equation of potassium permanganate decomposition. Calculate how many grammes of the salt have to be taken for the evolved oxygen to fill the gas meter up to two-thirds of its volume.

Weigh the required amount of potassium permanganate, transfer it into a glass retort provided with a rubber tube, and secure the retort in a stand.

Heat the retort with the potassium permanganate. When the air is displaced from the retort and the gas discharge tube, introduce the latter into the bottom opening of the gas meter for draining off the water. The water should flow into the sink. Fill the gas meter with oxygen (up to two-thirds of its volume), extract the gas discharge

tube, and close the bottom opening with a stopper. See that funnel *1* is filled with water. After the gas in the gas meter cools to room temperature, open cock *2* for a short time (for what purpose?).

The gas meter can also be filled with oxygen from a cylinder. Under what conditions is oxygen produced from barium peroxide and potassium chlorate? Write the equations of the reactions.

Obtaining a Stream of Oxygen from the Gas Meter. To fill a vessel with oxygen, pour water into it up to its rim, cover it with a glass plate coated with a thin layer of vaseline, invert it, and submerge the vessel in a bath with water. Remove the plate. Lower the gas discharge tube from the gas meter into the bath, open cocks *2* and *4*, and regulate the rate of oxygen supply. It should be such that the gas bubbles can easily be counted. Put the gas discharge tube under the opening of the vessel filled with water. When the vessel will be almost filled with oxygen, close it under the water with the glass plate and remove it from the water.

Why must a small amount of water be left in the vessel? What impurities does the gathered oxygen contain? Under what pressure is the gas in the gas meter?

4.2 PROPERTIES

1. Put a piece of sulphur the size of a pea into a spoon for burning, and ignite it in the flame of a burner (*in a fume cupboard!*). Note the colour and size of the flame of the burning sulphur. Introduce the burning sulphur into a jar with oxygen. What changes are observed in the burning of the sulphur?

2. Put a small piece of charcoal into a spoon for burning, heat it, and introduce it into a jar with oxygen. How will the intensity of burning of the charcoal change in the oxygen?

3. Fasten a steel wire coil to the end of a spoon for burning. Attach a piece of cork to the coil. Ignite the cork and rapidly introduce the coil with the cork into a jar with oxygen. What happens? Write the equation of the reaction in the molecular and electron forms. What conclusion on the properties of oxygen can be made on the basis of the above experiments? How does the replacement of air with oxygen change the intensity of burning of substances? How can this be explained? Why does oxygen have low melting and boiling points? What is the structure of an ozone molecule?

SUPPLEMENTARY EXPERIMENTS

OZONE

The Formation of Ozone in a Spark Discharge. Assemble an apparatus as shown in Fig. 40. Take a eudiometric tube with two platinum electrodes, fill it with water, and immerse it into a small cry-

stallizer filled with water. Introduce 5 ml of oxygen into the eudiometric tube. Connect the apparatus to a current source via a transformer and pass strong spark discharges through the tube. How will the volume of the gas in the eudiometric tube change?

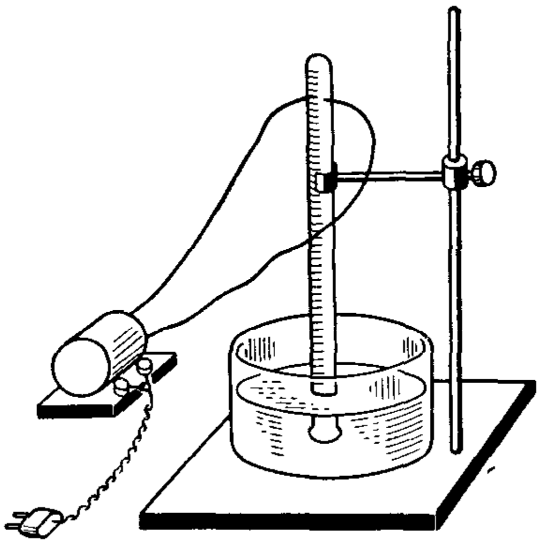


Fig. 40. An apparatus for producing ozone in a spark discharge

Preparation of Ozone in a Silent Electric Discharge. Assemble an apparatus as shown in Fig. 41. Pour concentrated sulphuric acid into the wash bottle, and distilled water into the cylinder. Switch on the induction coil, open the gas meter cocks, and pass a stream of oxygen through the ozonizer. What do you observe? Write the equation of the reaction of ozone formation.

Properties of Ozone. 1. Dissolve ozone in water. Does the solution have an odour?

2. Add two or three drops of a starch paste and the same volume of a potassium iodide solution to the obtained aqueous ozone solution. What is observed? Write the equation of the reaction.

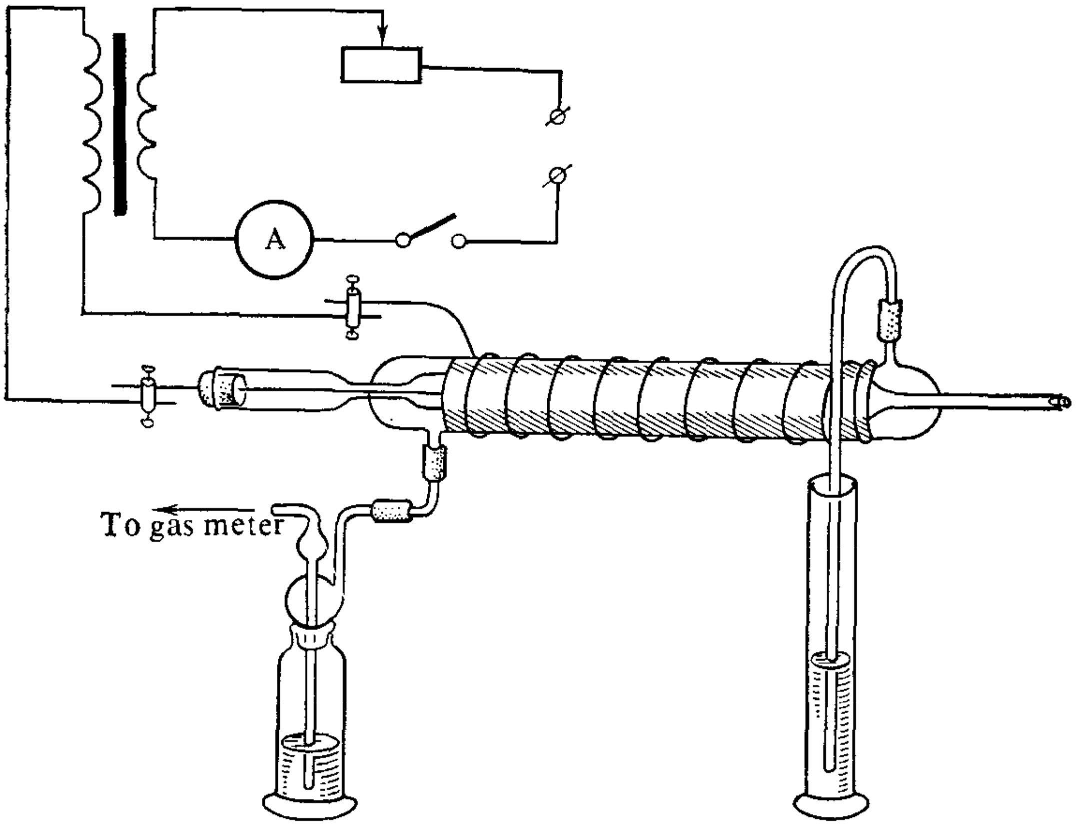


Fig. 41. An apparatus for producing ozone in a silent electric discharge

3. Pour an indigo solution into a beaker, lower the end of an ozonizer gas discharge tube into it, and pass a weak stream of oxygen through the ozonizer. What happens? What properties does ozone have? What is the structure of an ozone molecule?

5 HYDROGEN

Indicate the position of hydrogen in Mendeleev's periodic table of the elements, the structure and size of its atom, and its oxidation states. Write the electron configuration of a hydrogen molecule. What hydrogen isotopes are known?

Work with hydrogen requires great care! Hydrogen is flammable and when mixed with oxygen or air forms an explosive mixture. Perform all experiments in an atmosphere of hydrogen only in the presence of your instructor! Wear eye protection or a mask.

If hydrogen is to be heated in an apparatus or lit at its outlet, displace all the air from the apparatus prior to the experiment, next check the purity of the hydrogen (*in the presence of your instructor!*). To do this, prepare two test tubes. Fit a dry test tube onto the gas discharge tube, in 5-10 s slowly remove it while closing the test tube mouth with your thumb, and put the second test tube onto the gas discharge tube. Bring the inverted test tube filled with hydrogen up to the flame of a burner. Remove your thumb and light the hydrogen. By changing the test tube, check the purity of the evolved hydrogen until the gathered gas will light almost without a sound.

Only after being convinced in the purity of the evolving hydrogen may you ignite it with a burning splinter at the outlet of the apparatus from which it is evolving or begin to heat the apparatus (in the presence of your instructor!).

When conducting reactions in a hydrogen atmosphere in an apparatus being heated, stop the supply of the hydrogen only when the reaction part of the apparatus that was heated acquires a temperature close to the room one.

5.1 PREPARATION

Action of an Acid on a Metal. Assemble the setup shown in Fig. 42. Put 8-10 pieces of granulated zinc in the test tube, pour in 5 ml of a 20% sulphuric acid solution and close the tube with a stopper provided with a gas-discharge tube with its end drawn out upward. Check the purity of the hydrogen evolving.

After checking the purity of the evolving hydrogen (in the presence of your instructor!), ignite it with a burning splinter at the opening of

the gas-discharge tube. Put a cold inverted glass funnel over the hydrogen flame. What is observed? Write the molecular and electron equations of the reaction.

Action of an Alkali on Aluminium and Silicon. *(Perform the experiment in a fume cupboard, wear eye protection!)*

1. Put several pieces of aluminium into a test tube, and pour in 2-3 ml of a 20% sodium hydroxide solution. If the reaction proceeds slowly, heat the tube carefully. Determine what gas is evolved.

Write the molecular and electron equations of the reaction.

2. Put 0.2-0.3 g of amorphous silicon into a test tube and pour in 2-3 ml of a 20% sodium hydroxide solution. Does the reaction proceed in the cold? Gather the evolving gas and test it by bringing an

Fig. 42. A setup for producing hydrogen

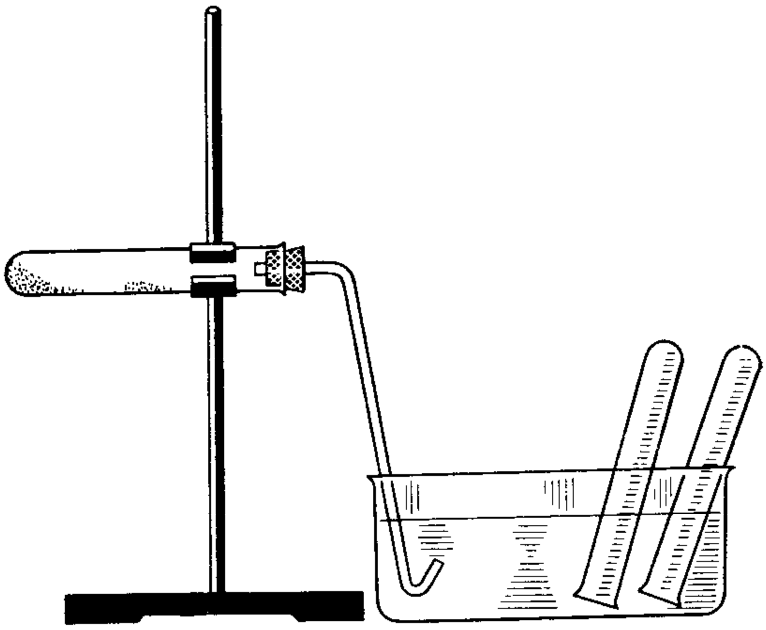


Fig. 43. A setup for producing hydrogen by the iron-steam method

ignited splinter up to the mouth of the tube. Write the molecular and electron equations of the reaction.

Reaction of a Metal with Water. 1. Fill a test tube with water up to its edges. Close its mouth with your thumb, invert it in a bath with water and fasten it in this position in the clamp of a stand. Wrap up several pieces of metallic calcium in cheese-cloth and rapidly place the metal under the tube with pincers. Determine what gas is evolved. Write the molecular and electron equations of the reaction.

2. Assemble the setup shown in Fig. 43 (the experiment is performed by two students). Pour a small amount of moist river sand onto the bottom of a dry refractory test tube, seeing that the tube

walls remain dry. Fasten the tube in the stand so that its bottom is slightly lower than its mouth. Make a narrow strip of paper into a groove and use it to pour a powder of reduced iron into the middle part of the tube. Close the test tube with a stopper accommodating a gas-discharge tube. Strongly heat the test tube with the flame of a gas burner where the iron is. Carefully heat the moist sand with the flame of a second burner. Gather the evolving gas over water and test its flammability. Write the molecular and electron equations of the reactions.

5.2 PROPERTIES

Preparation of Detonating Gas. (*Perform the experiment in the presence of your instructor!*) Measure the volume of a test tube and mark one-third of its volume with a rubber band. Pour water into the tube and transfer it into a bath with water. Fill one-third of the

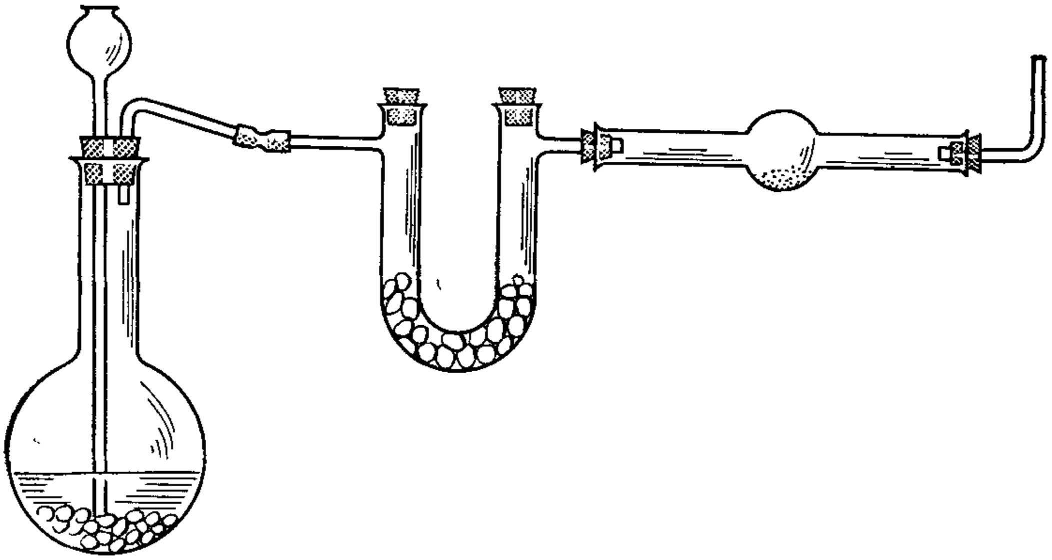


Fig. 44. An apparatus for studying the reduction properties of hydrogen

tube with oxygen from a gas meter and two-thirds with hydrogen from a Kipp gas generator.

Close the test tube under the water with your thumb, extract it from the bath, wrap it in a towel, bring it up to the flame of a burner and, after opening the test tube, light the gas mixture. What happens?

Reduction of a Metal Oxide (*wear eye protection*!). Assemble the apparatus shown in Fig. 44 and check its tightness. Put 40-50 pieces of granulated zinc into a 250-ml flask. Pour anhydrous calcium chloride into U-shaped tube. Put 0.3 g of copper oxide into the wide part of a refractory tube, and a piece of copper gauze or foil (why?) into the gas-discharge tube out of which hydrogen will flow. Pour 100-150 ml of a 20% sulphuric acid solution into the flask. Again check

the tightness of the apparatus (how can this be done?) Check the purity of the evolving hydrogen (*in the presence of your instructor!*). *Having convinced yourself that the hydrogen is pure, light the hydrogen at the outlet opening of the apparatus with a match.* Carefully heat the reaction tube along its entire length and then strongly heat the part of the tube where the copper oxide is. See that the flame of the burning hydrogen does not diminish. If the flame extinguishes, stop heating (*in the presence of your instructor!*).

When reduction is completed (how can this be established?), stop the heating and cool the apparatus to room temperature in a hydrogen stream (why?). Hand in the reduced copper to your instructor. Wash the unreacted zinc with water and hand it in to the laboratory assistant.

5.3 HYDROGEN PEROXIDE

Preparation. Pour 20 ml of a 5% sulphuric acid solution into a 50-ml flask and cool it to 0 °C. While shaking the contents of the flask during 5-10 min, add about 1 g of barium peroxide in small portions. Filter the obtained hydrogen peroxide solution from the precipitate. Study the properties of hydrogen peroxide.

Properties. 1. Introduce manganese(IV) oxide into a test tube containing a hydrogen peroxide solution. What gas is evolved? What role is played by the manganese(IV) oxide? Write the equation of the reaction.

2. Pour several drops of a potassium iodide solution into a hydrogen peroxide solution. What is observed? Dilute the solution with water and add one or two drops of a starch solution to it. What happens? Write the molecular and electron equations of the reaction.

3. Prepare a lead sulphide precipitate by reacting solutions of a lead salt and ammonium sulphide. Treat a small amount of the precipitate, washed with water by decantation, with a hydrogen peroxide solution. Why does the colour of the precipitate change? Write the equations of the reactions. What properties does hydrogen peroxide exhibit in this and the preceding reactions?

4. Add a hydrogen peroxide solution to a potassium permanganate solution acidified with sulphuric acid. Comment on your observations. Write the molecular and electron equations of the reaction. What properties of hydrogen peroxide does this reaction indicate?

6 RATE OF CHEMICAL REACTIONS

6.1 RATE OF HOMOGENEOUS REACTIONS

What factors determine the rate of a chemical reaction? Give examples of reactions proceeding at various rates.

EFFECT OF REACTANT CONCENTRATION ON REACTION RATE

Reaction of Sodium Thiosulphate with Sulphuric Acid. Pour 10 ml of a 2.5% sulphuric acid solution into each of four small beakers, and a 5% sodium thiosulphate solution and water into four other beakers in the following proportions:

Beaker No	1	2	3	4
Sodium thicsulphate, ml	10	20	30	40
Water, ml	30	20	10	0

Measure the volumes of the solutions as accurately as possible and pour them together in pairs. Use a stop watch or a metronome to note the time interval after which turbidity appears. What is the turbidity of the solution caused by? Write the equations of the reactions. Enter the results in your laboratory notebook using Form 7.

Form 7. REACTION OF SODIUM THIOSULPHATE WITH SULPHURIC ACID

Experiment No.	Volume of solution, ml		Volume of water, ml	Total volume, ml	Time, s
	Sulphuric acid	Sodium thiosulphate			

The concentration of which substance and how many times changes from one experiment to another? What conclusion should be made from the data of the experiments? How does the reaction rate depend on the reactant concentration?

Reaction of Potassium Iodate with Sodium Sulphite in a Sulphate Medium. Pour 20 ml of a sodium sulphite solution acidified with sulphuric acid and containing a small amount of starch into a 100-ml beaker. Pour 20 ml of a potassium iodate solution into a second 100-ml beaker. The potassium iodate solution must contain

3.9 g of the salt per litre of solution, and the sodium sulphite solution must contain 1 g of the salt, 0.95 ml of sulphuric acid (a 96% solution), and 0.1 g of starch per litre of solution. Rapidly pour the second solution into the first one. Note the time of pouring the solutions together and the instant when a colour appears. Write the equation of the reaction.

Repeat the experiment, halving the concentration of the second solution (take 10 ml of the initial solution and 10 ml of water). Enter the results in your laboratory notebook, using Form 8.

Form 8. REACTION OF POTASSIUM IODATE WITH SODIUM SULPHITE

Experiment No.	Volume of solution, ml		Total volume, ml	Time, s
	potassium iodate	sodium sulphite		

How does the change in the reactant concentration affect the rate of the chemical reactions?

EFFECT OF CATALYST ON REACTION RATE

Decomposition of Hydrogen Peroxide in the Presence of Potassium Dichromate (the experiment is performed by two students). Assemble the apparatus shown in Fig. 45. Fill the burette with water up to its zero graduation. Close the burette opening with your thumb, invert the burette, and immerse it in a bath with water. Fasten the burette in the stand and note the level of the water in it. Maintain a constant temperature of the water in the bath (25 °C), for which purpose add hot water to it from time to time.

Measure 30 ml of a 0.2% potassium dichromate solution with a measuring glass and pour it into a reaction flask. Pour 20-25 ml of a 0.2% hydrogen peroxide solution into another flask. Put both flasks into the bath of the apparatus and keep them there during

Form 9. DECOMPOSITION OF HYDROGEN PEROXIDE IN THE PRESENCE OF POTASSIUM DICHROMATE

Experiment No.	Time, s	Reading of burette, ml	Volume of oxygen evolved during 30 s, ml

15-20 min to let the solutions acquire the temperature of the bath. Take 5 ml of the hydrogen peroxide solution with a pipette and pour it into the reaction flask containing the potassium dichromate. What do you observe?

Close the flask with a stopper provided with a gas-discharge tube, bring the latter under the burette, and while continuously and uniformly shaking the flask (without extracting it from the bath), note the volume of the evolved oxygen every 30 s. Note the colour of the solution when the process terminates. Perform at least 15-20 measurements. Enter the results in your laboratory notebook using Form 9.

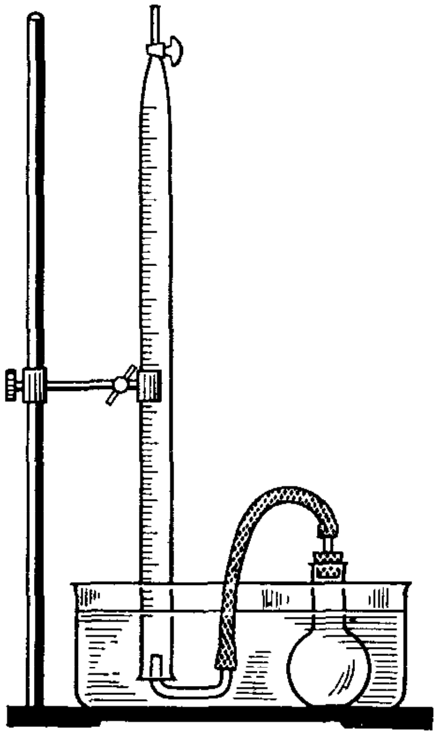


Fig. 45. An apparatus for studying the decomposition of hydrogen peroxide in the presence of potassium dichromate

While uniformly shaking the reaction flask, the first student takes the readings of the burette according to signals of the second student—"Attention! Reading!". The second student watches the time and enters the readings in Form 9. The fourth column can be filled in after completing the experiment.

Use the data obtained to plot a curve of the volume of oxygen evolved every 30 seconds versus the time.

Run a similar experiment with 5 ml of hydrogen peroxide without the potassium dichromate solution, using the same volume of water instead of it. Compare the results of the experiments. What is the role of potassium dichromate? What are such substances called?

EFFECT OF TEMPERATURE ON REACTION RATE

Pour 10 ml of a 2.5% sulphuric acid solution into each of three dry beakers, and 10 ml of a 5% sodium thiosulphate solution into each of three other beakers. Measure the volumes as accurately as possible, using small measuring cylinders or burettes. Run the first experiment at room temperature. Rapidly pour the sulphuric acid solution into the sodium thiosulphate one. Record the time of pouring the solutions together with the aid of a stop watch or a metronome. Consider the instant when a hardly noticeable turbidity appears at the end of the reaction.

Run a second experiment like the first one, but at a temperature 10 °C higher than room temperature. For this end, heat the next pair of beakers in a water bath whose temperature is controlled by means of a thermometer. Keep the solutions in the bath during 15-20 min, and then pour them together. What is observed?

Run a third experiment at a temperature 20 °C higher than room temperature, heating the solutions as indicated above. Enter the results in your laboratory notebook using Form 10.

Form 10. EFFECT OF TEMPERATURE ON REACTION OF SULPHURIC ACID WITH SODIUM THIOSULPHATE

Experiment No.	Volume of solution, ml		Temperature, °C	Time, s (or number of metronome beats up to appearance of turbidity)
	sulphuric acid	sodium thiosulphate		

How does the change in the temperature affect the rate of the chemical reaction?

6.2 RATE OF HETEROGENEOUS REACTIONS

EFFECT OF THE DEGREE OF REACTANT MIXING ON THE REACTION RATE

Put about 0.01 g of anhydrous copper sulphate and several crystals of potassium iodide into a dry porcelain mortar. Mix these substances with a pestle, and then triturate them. What do you observe? Add a few drops of water to the mixture. Explain the observed phenomena. Write the equation of the reaction.

What factors affect the rate of homogeneous and heterogeneous chemical reactions? What is called the order of a reaction? Give examples of first- and second-order reactions. Write a mathematical expression of the law of mass action for a first- and second-order irreversible reactions.

What is the physical meaning of the rate constant of a chemical reaction? What is the dimension of the rate constant of a first- (second-) order chemical reaction? How does the rate constant depend on the temperature? Write the Arrhenius equation. What is called the activation energy? What substances are called catalysts and inhibitors?

SUPPLEMENTARY EXPERIMENTS

1. Effect of the Surface Area on the Reaction Rate. Assemble an apparatus as shown in Fig. 45. Introduce 0.1 g of powdered metallic zinc into a 50-ml reaction flask and pour in 10 ml of a 20% sulphuric acid solution. Put the end of the gas-discharge tube under the burette and determine the volume of hydrogen that evolves during two to five minutes. Perform the experiment at a constant temperature, shaking the reaction mixture. Why?

Run the same experiment, using 0.1 g of zinc in the form of pieces or plates. Repeat similar experiments with magnesium, taking it in an amount of 0.04 g and using a 10% sulphuric acid solution instead of the 20% one. How does the surface area of the reactants affect the rate of the chemical reaction proceeding in a heterogeneous medium?

2. Effect of Light on the Decomposition of Silver Chloride. Introduce 2 ml of a 0.1 *N* silver nitrate solution into a test tube and add dropwise such an amount of a saturated sodium chloride solution that will be sufficient for the complete precipitation of the silver as a chloride. Rapidly filter out the precipitate, rinse it with water and put it on two watch glasses. Place one glass with the precipitate in a dark cupboard, and leave the other at a window in daylight. In an hour, compare the colour of the precipitates and explain the phenomena you observe. How does light affect the reaction? After the experiment, put the precipitates containing a silver compound into the jars set aside for them.

7 CHEMICAL EQUILIBRIUM

What reactions are called practically reversible ones?

What are the conditions of irreversibility and reversibility of chemical reactions?

What state is called that of chemical equilibrium and why is it dynamic? What factors shift chemical equilibrium? State the le Châtelier principle.

7.1 EFFECT OF REACTANT CONCENTRATION

Reaction of Iron(III) Chloride with Ammonium Thiocyanate. Prepare for this experiment a 0.01-0.02 *M* solution of iron(III) chloride and a 0.02-0.03 *M* solution of ammonium thiocyanate. Pour into a beaker 20 ml each of the iron(III) chloride and ammonium thiocyanate solutions. How can the red colour of the solution be

explained? Write the equation of the reaction. Does the given reaction proceed to the end?

Pour the solution obtained into four test tubes. Keep the first one as a reference. Add to the second tube two or three drops of a concentrated iron(III)] chloride solution, to the third one two or three drops of a concentrated ammonium thiocyanate solution, and to the fourth one a small amount of dry ammonium chloride. Stir the contents of the test tubes and observe the change in the intensity of the colour of the solutions.

Explain the occurring phenomena on the basis of the law of mass action. Will equilibrium be shifted if the obtained solutions are diluted? The concentration of what substance changes from one experiment to another, and how many times? What conclusion should be made from the results obtained?

7.2 EFFECT OF TEMPERATURE

Thermal Dissociation of Nitrogen(IV) Oxide. Use two communicating flasks filled with nitrogen(IV) oxide for this experiment (Fig. 46). Immerse flask *1* into a beaker filled with snow or crushed ice, and flask *2* into a beaker with water. Heat the latter and watch the change in the colour of the gas in both flasks. Extract the flasks from the beakers. How does the colour of the gas change?

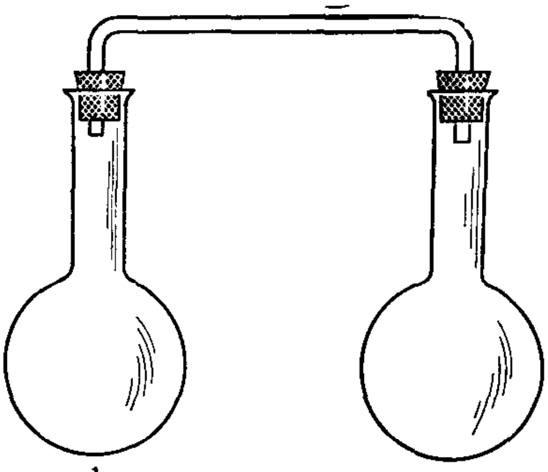


Fig. 46. A setup for studying the thermal dissociation of nitrogen(IV) oxide

Give the thermodynamic derivation of the law of mass action for the reaction $A + B \rightleftharpoons C + D$.

What is the physical meaning of the chemical equilibrium constant? What factors does it depend on?

Write a mathematical expression for the temperature dependence of the chemical equilibrium constant of reactions proceeding in the gaseous phase (K_p), (K_v), and in an aqueous solution (K_c).

SUPPLEMENTARY EXPERIMENT

Reaction of Potassium Chloride with Nitric Acid. Put 1 g of sodium or potassium chloride in a porcelain bowl and add 10 ml of a concentrated nitric acid solution. Put the bowl in a water bath in a fume cupboard and evaporate until dry. Dissolve a small part of the dry residue in water and test the solution with silver nitrate.

Repeat the evaporation until a dry residue is obtained two or three times using the same amount of nitric acid as previously, and test the dry residue each time for the presence of the chloride. What do these experiments show? Write the equation of the occurring reaction.

Evaporate the obtained salt with 10 ml of concentrated hydrochloric acid in a water bath until dry. Dissolve a small sample of the dry residue in water and test it with silver nitrate. Explain the phenomena that occur.

8 SOLUTIONS

8.1 SOLUBILITY OF SALTS

Determining the Solubility of Potassium Dichromate. Prepare a potassium dichromate solution that is saturated at room temperature. Using the table of solubility (see Appendix 1, Table 1), calculate the amount of potassium dichromate needed for the saturation of 50 ml of distilled water, and take an excess of it (10%). Place the amount of salt weighed on a technical chemical balance in a 100-ml flask and add 50 ml of distilled water to it. Close the flask with a stopper and stir its contents during 10-15 min (better in a shaker) while holding the flask by its neck. Prior to filtration, measure the temperature of the solution. Filter off the remaining insoluble salt and gather the filtrate in a dry flask.

Thoroughly wash a burette with a chromium mixture and water, and then rinse it two or three times with the prepared saturated potassium dichromate solution. Why is this done? Fasten the burette in a stand and pour the transparent solution into it. Fill the tip of the burette with the solution and note the level of the liquid in the burette.

Weigh a porcelain bowl with an accuracy up to 0.1 g on a technical chemical balance. Pour about 20 ml of the solution from the burette into the weighed bowl. Determine the volume of the solution with an accuracy up to 0.1 ml. Weigh the bowl with the solution. Evaporate the solution until dry on a water bath. Place the bowl with the substance in a drying cabinet. How can you determine that the precipitate has been dried?

Weigh the bowl with the dry potassium dichromate. Transfer the residues of the potassium dichromate and its solutions into special jars (take them from the laboratory assistant). Enter the results of your measurements and weighings into your laboratory notebook, using Form 11.

Form 11. DETERMINING THE SOLUBILITY OF POTASSIUM DICHROMATE

Item	Experiment No.	
	1	2
Temperature of saturated solution, °C		
Level of solution in burette after pouring solution out, ml		
Ditto, before pouring solution out, ml		
Volume of solution taken for evaporation, ml		
Mass of porcelain bowl with solution, g		
Mass of empty porcelain bowl, g		
Mass of solution, g		
Mass of porcelain bowl with dry salt		
Amount of potassium dichromate contained in the taken solution, g		

Find the mass of potassium dichromate that saturates 100 g of water, 100 g of solution, and 1000 ml of solution at the noted temperature. How can the solubility of substance be expressed?

8.2 EFFECT OF TEMPERATURE ON SALT SOLUBILITY

Aluminium Potassium Alum. Put about 2 g of aluminium potassium alum into a test tube containing 3 ml of water. Does the alum dissolve in this amount of water in the cold? If it doesn't, heat the contents of the tube almost to boiling. What is observed? Let the solution cool. What happens? How does the solubility of the alum change with a change in the temperature?

Sodium Chloride. Dissolve about 2 g of sodium chloride in 3 ml of water with heating. Pour the transparent hot solution into a dry test tube. What do you observe when the solution cools?

Calcium Acetate. Pour a small amount of a saturated calcium acetate solution into a dry test tube and heat it. Next cool the solution with a stream of water from a faucet. What is observed?

Find the values of the solubility (Appendix 1, Table 1) of alum, sodium chloride, and calcium acetate, and draw curves of their temperature dependence, laying off the temperature along the axis of abscissas and the concentration of a saturated solution along the axis of ordinates.

Acquaint yourself with the appearance of aluminium potassium alum, sodium chloride, and calcium acetate crystals using a microscope. To do this, transfer a drop of the relevant solution containing a few crystals onto a slide. Cover the liquid with a cover glass and place the preparation on the microscope stage. Draw the shape of the crystals.

8.3 PREPARATION OF SUPERSATURATED SOLUTIONS

Copper Sulphate Pentahydrate. Calculate what amount of copper sulphate crystallohydrate (blue vitriol) has to be taken for 10 ml of water to prepare a solution saturated at 60 °C (see Appendix 1, Table 1). Bring the solution obtained at the indicated temperature almost up to boiling and rapidly filter it through a fluted filter on a funnel for hot filtration (the funnel must be hot). Close the test tube with the filtrate with a piece of cotton wool. If crystals have formed in the filtrate, dissolve them by careful heating. Cool the solution and introduce a minute crystal of the initial salt into it. What is observed? Does the temperature of the solution change?

Heat the test tube with its contents to obtain a transparent solution again, carefully cool it, and rub the inner wall of the test tube containing the solution with a glass rod. Explain the precipitation of crystals. Give definitions of saturated, unsaturated, and supersaturated solutions.

Sodium Thiosulphate. Put several salt crystals into a dry test tube and heat it very slowly. What happens? Close the tube with cotton wool and let it cool. Vigorously agitate the tube cooled to room temperature. What do you observe?

Heat the tube with the salt to obtain a transparent solution again. Cool it and introduce a minute crystal of the initial substance into it. Describe the phenomenon you observe.

8.4 THERMAL PHENOMENA IN DISSOLUTION OF SALTS

Observe the thermal phenomena occurring when 0.1 mol of the following salts is dissolved in 50 ml of water: ammonium nitrate, anhydrous sodium sulphate, and sodium sulphate decahydrate (Glauber salt). For this purpose, pour 50 ml of water into a 100-ml beaker, measure its temperature, and, after pouring in the relevant amount of a salt, see how the temperature changes. Explain what occurs.

Draw curves of the solubilities of the indicated salts. What relation can be noted between the heat of dissolution of a substance and the change in its solubility with the temperature?

SUPPLEMENTARY EXPERIMENTS

1. Change in Volume in Dissolution. *Dissolution of Sodium Chloride in Water.* Weigh 21 g of sodium chloride. Calculate the volume occupied by the given amount of salt using a table of the density of substances (see Appendix 1, Table 4). Pour 90 ml of water into a

100-ml measuring cylinder, and introduce a glass rod and a thermometer into it. Note the level of the water in the cylinder and its temperature. Carefully pour in the weighed salt using a dry funnel so that the salt does not get onto the walls of the cylinder. By stirring with the rod, achieve complete dissolution of the salt. When the solution acquires room temperature, note its volume.

Dissolution of Ammonium Chloride in Water. Weigh 21 g of ammonium chloride, calculate its volume, and dissolve it in 150 ml of water, proceeding in the same way as in the preceding experiment. Note the volume of the solution obtained.

Dissolution of Sugar in Water. Take 50 g of sugar and dissolve it in 250 ml of water. Measure the volume of the solution.

Dissolution of Ethanol in Water. Pour 4 ml of water into a 10-ml measuring cylinder. Put a thin glass rod into it and note the level of the liquid in the cylinder. Add 4 ml of water and again note the level. Pour out the water. Again pour 4 ml of water and 4 ml of absolute ethanol into the cylinder and thoroughly mix the liquid with the rod. What is observed? Enter the data of all the experiments in your laboratory notebook using Form 12.

Form 12. CHANGE IN VOLUME IN DISSOLUTION

Experiment No.	Substance being studied	Volume, ml		Mass of substance, g	Density of substance, g/cm^3	Volume of substance, ml	Total volume of solution with glass rod, ml		Deviation from sum of volumes of substances taken	
		water	water and glass rod				calculated	found	± ml	±%

What conclusions can be made from the experiments performed?

2. Determining Solubility of Air in Water. Assemble an apparatus (Fig. 47) so that the end of the tube does not emerge from the stopper. The volume of the flask should be 250-300 ml. Check the tightness of the apparatus. Measure the volume of the flask up to the stopper.

Pour about 350 ml of distilled water into a flask with a volume of 0.5-1 litre and saturate it with air by shaking it. Fill the flask of the apparatus and the gas-discharge tube with the water saturated with air. Close the flask, making sure that not a single air bubble remains in the flask and in the tube. Put a test tube filled with water onto the free end of the gas-discharge tube immersed in a bath with water and fasten it in a stand (the test tube and the stand are not shown in

the figure). Measure and record the temperature of the water saturated with air and the atmospheric pressure. Heat the water and boil it up to complete evolution of the gases from it (5-8 min). When the gas stops evolving, extract the gas-discharge tube from the water,

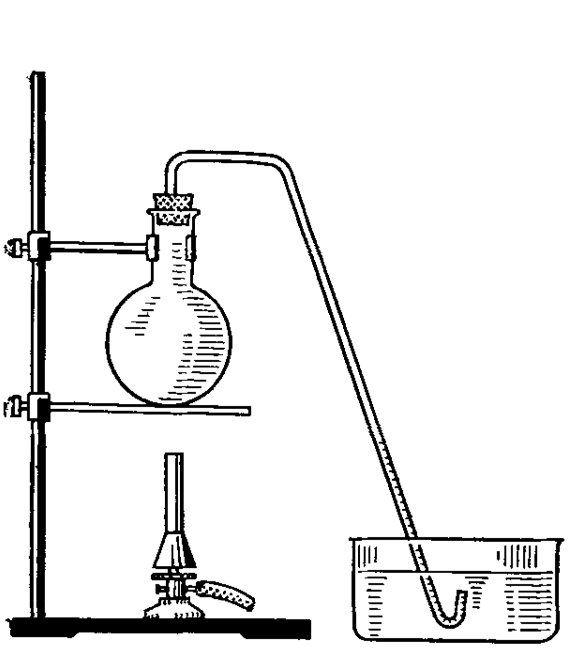


Fig. 47. An apparatus for determining the solubility of gases in water

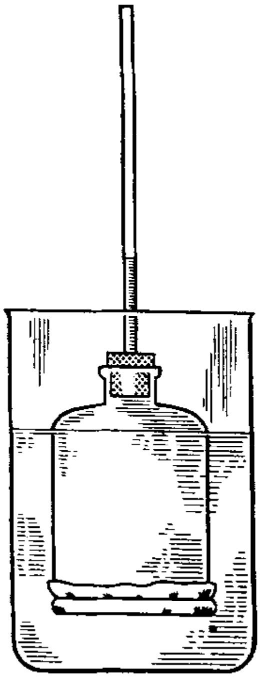


Fig. 48. Setup for observing osmosis

and cool the test tube with the collected gas to the temperature at which the water was saturated with air.

Adjust the pressure of the gas in the test tube to atmospheric, mark the level of the water with a rubber band, and determine the volume of the evolved gas with a small measuring glass. Enter the results in your laboratory notebook using Form 13.

Form 13. DETERMINING SOLUBILITY OF AIR IN WATER

Volume of water in flask, ml	Volume of evolved gas under given conditions, ml	Atmospheric pressure of gas, mmHg	Temperature, °C	Water vapour pressure, mmHg

Calculate the volume of dry air that was dissolved in the water under the conditions of the experiment. How does the solubility of gases change with a change in the pressure? What was the composition of the gas that evolved from the water?

3. Osmosis. Assemble the setup shown in Fig. 48. Cover the wide opening of a glass vessel that is a bottomless jar with an animal blad-

der, cellophane, or a collodion film (see p. 171). Fill the vessel with a concentrated sugar solution and close its upper narrow opening with a rubber stopper accommodating a long narrow tube. Part of the solution will enter the tube. Immerse the setup into a bath with distilled water, note the level of the liquid in the tube, and observe how the liquid rises. Why does the liquid rise in the tube and how long will this occur? What is called osmosis and osmotic pressure? How does the osmotic pressure depend on the temperature and the solute concentration? State van't Hoff's law.

4. Determining the Freezing Point of Water. (a) To determine the freezing point of substances, use an arrangement as shown in Fig. 49. Thoroughly wash test tube *1* and stirrer *2*. Secure thermometer *3* so that it fails to reach the bottom of the test tube by 1-2 cm (the thermometer must have graduations of 0.01 °C). Pour in an amount of distilled water such that its level is 2-3 cm higher than the top of the mercury bulb of the thermometer. Submerge tube *1* directly into beaker *4* filled with a cooling mixture (see Appendix 1, Table 17) whose temperature should be 2-3 °C below the freezing point of water. Watch the change in the temperature while constantly stirring the water with stirrer *2*. Take the readings of the thermometer every 10 seconds. How is the drop, elevation, constancy, and new drop of the temperature when the water is cooled explained? Draw a graph of the change in the temperature with time. At what temperature did the water freeze?

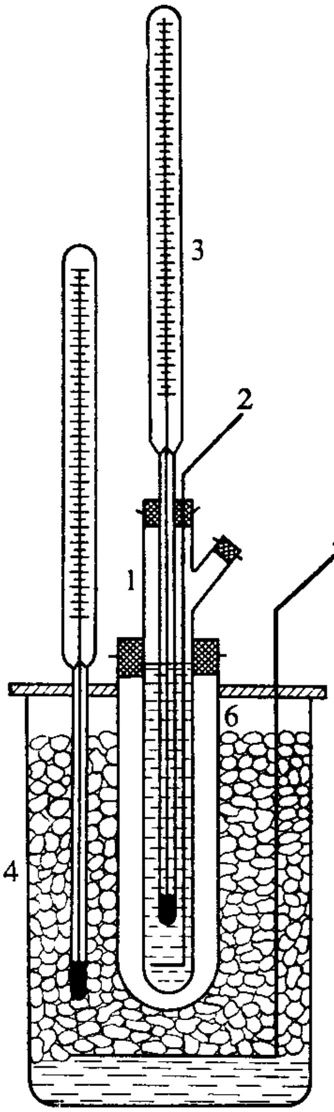


Fig. 49. Arrangement for determining the freezing point of substances

Draw a phase diagram of water. What is called a phase, component, and degree of freedom? How many phases and degrees of freedom are there at different points of the phase diagram of water? What is known as the freezing (boiling) point of pure substances?

(b) More accurate results can be obtained as follows. Immerse test tube *1* containing the required ámount of water into test tube *6* placed

in beaker *4* with the cooling mixture. Stir the cooling mixture and the water with stirrers *2* and *5* until the temperature of the water lowers to a value exceeding the previously found approximate value of its freezing point by 0.5 °C. Again begin stirring. While watching the temperature, note its maximum elevation—the freezing point of water. Repeat this determination two or three times.

5. Determining the Temperature of Water Crystallization from Aqueous Sugar and Sodium Chloride Solutions. Weigh empty test tube *1* (Fig. 49) with an accuracy up to 0.1 g, and then weigh it with water. Calculate what amount of sugar and sodium chloride has to be added to the taken amount of water to prepare unimolal solutions. Weigh the calculated amount of substance with the same accuracy in a preliminarily weighed weighing bottle, transfer it into test tube *1* so that the substance gets only into the solvent, and not onto the tube walls. Weigh the test tube with the solution again. Determine first approximately, and then accurately the temperature of the beginning of crystallization of water from aqueous solutions of sugar and sodium chloride.

Plot the change in the saturated vapour pressure of water over pure water and an aqueous solution of sugar (sodium chloride) against the temperature. How does the freezing (boiling) point of water change when it contains solutes (sugar, sodium chloride)? Define the cryoscopic and ebullioscopic constants of water. What is their numerical value? State Raoult's laws and write their mathematical expression. How can the molecular masses of solids be determined?

6. Determining the Cryohydrate Point. (This experiment is performed by two students.) Prepare a cooling mixture that freezes at —30 °C (see Appendix 1, Table 17) and put it into the beaker of an arrangement for determining the freezing point of solutions (see Fig. 49). Pour a unimolal barium chloride solution into test tube *1* with an offtake and put tube *1* into larger test tube *6*. Watch how the temperature changes while constantly stirring the solution with stirrer *2*. Note the readings of the thermometer every 10 seconds. Lower the temperature to —15 °C. Extract the test tube with the barium chloride solution from the cooling mixture and note the temperature of the reaction mixture every 10 seconds. Plot the temperature against the time.

How can the shape of the temperature-time curve be explained? Define the eutectic point (cryohydrate point).

9 ELECTROLYTIC DISSOCIATION

State the fundamental propositions of the theory of electrolytic dissociation.

9.1 ELECTRICAL CONDUCTANCE OF SOLUTIONS

Pour 50 ml of a 0.1 *N* aqueous or ethanol solution of potassium hydroxide or potassium nitrate into four 100-ml beakers (use two of them for each solvent). Using a stationary setup for determining the electrical conductance (Fig. 50), check whether these solutions conduct an electric current. For this purpose, immerse the carbon electrodes into a beaker with the relevant solution and observe the reading of the ammeter. See that the electrodes are always immersed to the same depth. When transferring the electrodes from one solution into another one, wash them with distilled water.

What explains the different electrical conductance of an aqueous and ethanol solutions of the same substance in the same concentration (*N*)? What is called the dielectric constant (permittivity)?

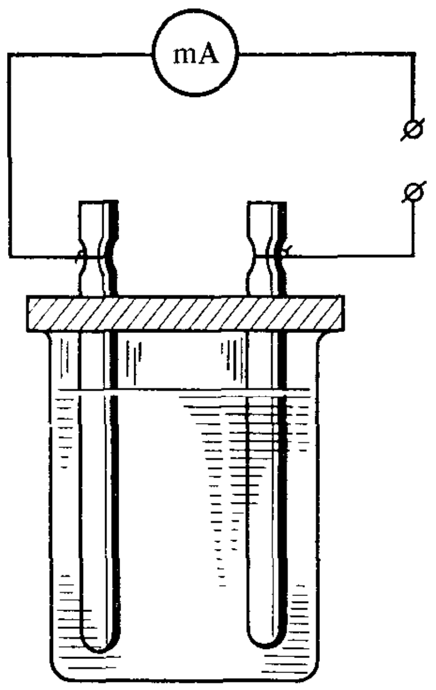


Fig. 50. Setup for determining the electrical conductance of solutions

9.2 COMPARISON OF THE STRENGTH OF ACIDS AND BASES

What classes of chemical compounds are called acids, bases, and salts?

Change in the Colour of Indicators in Acid and Alkaline Solutions. Pour 2-3 ml each of 1 *N* solutions of hydrochloric and acetic acids, sodium hydroxide, and an aqueous ammonia solution into test tubes. Pour one or two drops of a phenolphthalein solution into each of the tubes and see whether the colour of the solution changes. Perform similar experiments with other indicators, namely, methyl red, litmus, methyl orange (see Appendix 1, Table 6). Enter your observations into your laboratory notebook using Form 14.

Form 14. CHANGES IN INDICATOR COLOURS

Substance being tested	Indicator	Colour of solution

Preparation of Acid Solutions of the Same Normality. Prepare 100 ml each of 1 *N* solutions of sulphuric, hydrochloric, and acetic acids, using concentrated solutions of the acids (see Appendix 1, Table 2). Pour these solutions into burettes with an indication of their density or concentration in per cent.

Measuring flasks of various volumes are used to prepare solutions with an exact concentration. Thoroughly wash the flask in which a solution is to be prepared with a chromium mixture (see p. 22).

Pour 40-50 ml of distilled water into a flask, then add the calculated amount of the initial concentrated acid, and after stirring and cooling add water up to the mark. Close the flask with a stopper and thoroughly stir the solution by turning the flask upside down and back and shaking it.

Determining the Concentration of Acid Solutions by Titration. Titration is used to accurately determine the concentration of solutions. To the acid solution being investigated, add an alkali solution of an exactly known concentration (a titrated solution) up to neutralization. The instant of neutralization is established according to the change in the colour of the indicator (phenolphthalein, methyl red, methyl orange).

Titrated solutions are stored in large bottles with burettes connected to them (Fig. 51). First fill the burette with the solution above the zero graduation, and then drain off the liquid to this graduation, generally adopted as the beginning of measurement. See that there are no air bubbles in the tip of the burette. When reading the level of the solution in the burette, keep your eyes at the lower edge of the liquid meniscus.

Introduce 10 ml of a prepared acid with a pipette into each of two conical 100-ml flasks and add two or three drops of a phenolphthalein indicator. A liquid is generally drawn into a pipette by using a slight vacuum, for example, with the aid of a rubber bulb or a rubber tube connected to a water-jet pump. *Never suck in a liquid with your mouth.* Using a wash bottle with distilled water, wash off the drops of the acid solution from the walls of the conical flask and perform titration. Add the alkali to the acid in small portions, continuously stirring the solution. Hold the neck of the flask with the fingers of your right hand, and open the burette clamp with your left hand. The end of titration is determined by the appearance of a hardly noticeable crimson colour (phenolphthalein) that does not vanish during 30 seconds, or by the change in colour of the relevant indicator used (methyl orange, methyl red). Note the reading of the burette with an accuracy up to 0.05 ml and add another drop of the alkali solution. The appearance of a quite noticeable colour of the solution indicates that the last drop was excessive.

Again fill the burette with an alkali solution up to the zero graduation and repeat the titration of the acid in the second flask.

The tolerated discrepancy between the two measurements is 0.05 ml. It is recommended to enter the results in your laboratory notebook using Form 15.

Form 15. DETERMINING THE CONCENTRATION OF ACID SOLUTIONS BY TITRATION

Name of acid	Experiment No.	Volume of solution, ml		Concentration, *N*	
		acid	alkali	alkali	acid

Calculate the normality of the prepared acid from the data obtained. Write the molecular and net ionic equations of the neutralization reaction.

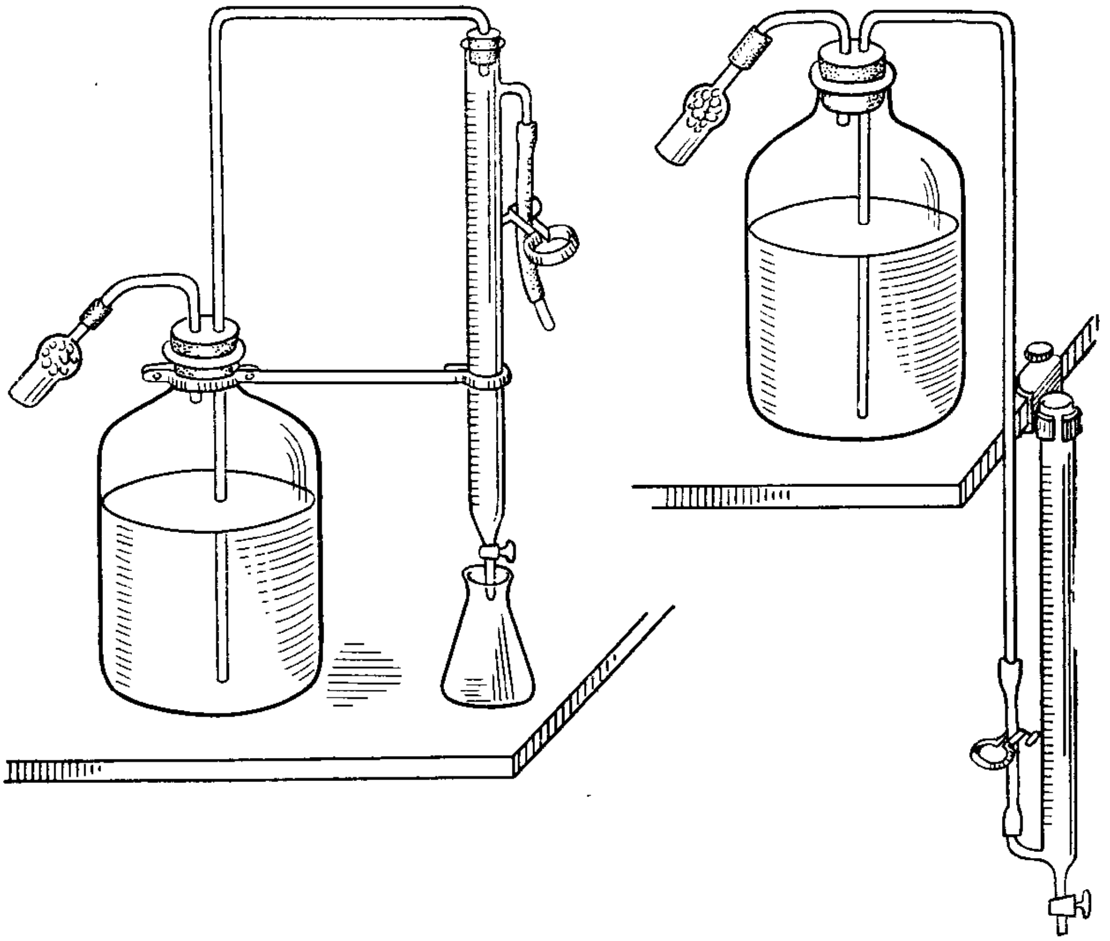


Fig. 51. Large bottles and burettes for titrated solutions

What is the essence of a neutralization process? How can the neutrality of a solution be determined? At what hydrogen ion concentration is a reaction neutral? What is the ion product of water? What is the value of the ion product of water at 22 °C? In what volumes

will an alkali react with an acid at an identical normality of their solutions? Is such a relation observed for acid and alkali solutions with the same concentration in per cent?

Electrical Conductance of Acid Solutions. Pour prepared acid solutions into three dry beakers and check whether they conduct an electric current. Record the ammeter readings. On the basis of these experiments, arrange the acids in a series according to their activity.

How Acids with the Same Normality Affect a Metal. Pour identical amounts (10 ml) of 1 *N* hydrochloric, sulphuric, and acetic acid solutions into three test tubes. Take three identical pieces of magnesium (not over 0.2 g) or identical masses (not over 0.2 g) of basic copper carbonate and simultaneously introduce them into the tubes with the acids. Note in which acid the magnesium (or carbonate) dissolves more rapidly. Why?

Electrical Conductance of Aqueous Solutions of Ammonia and Metal Hydroxides. Check the electrical conductance of 1 *N* solutions of sodium hydroxide, potassium hydroxide, and ammonia. Record the ammeter readings. Arrange the studied alkalies in a series according to their activity. Acquaint yourself with the degree of dissociation and the dissociation constants of acids and bases (see Appendix 1, Tables 9 and 10). Why is the term "apparent degree of dissociation" used to characterize the dissociation of strong electrolytes?

9.3 CHANGE IN THE HYDROGEN AND HYDROXYL ION CONCENTRATION

1. Pour 5 ml of a 1 *N* hydrochloric acid solution into a test tube and throw a small piece of zinc into it. When the evolution of hydrogen becomes quite vigorous, add 1-2 g of sodium acetate. Explain the change in the rate of hydrogen evolution. Write the molecular and net ionic equations of the chemical reaction of hydrochloric acid with sodium acetate. Does the activity of acetic acid decrease when dry sodium acetate is added to its solution?

2. Pour 3 ml of a 1 *N* alkali solution into each of two test tubes. Add about 1 g of solid ammonium chloride to one of them and dissolve it by shaking the tube. Pour 2 ml of a magnesium chloride solution into both tubes. Why does no precipitate form in one case? Explain the observed phenomenon proceeding from the change in the hydroxyl ion concentration.

3. Pour 3 ml of a 0.1 *N* ammonia solution into each of two beakers. Add dry ammonium chloride to one beaker until the solution is saturated. Pour 2-3 ml of a magnesium chloride solution into both beakers. Explain the observed phenomenon using the law of mass action.

Which electrolytes are called strong, and which are called weak? In what form can the law of mass action be applied to strong electrolytes? Define the activity, the activity coefficient, and the ionic strength of a solution.

Determining the pH of Solutions. (It is desirable to use a pH-meter in these experiments.) Using a universal indicator (or a pH-meter), determine the pH of water and 0.1 *N* solutions of hydrochloric, acetic, and phosphoric acids, and of sodium and ammonium hydroxides.

Do acid solutions of the same normality differ in their pH? What is the relation between the hydrogen ion concentration and the pH of solutions? See whether the pH of solutions of phosphoric and acetic acids and of ammonia will change when dry sodium phosphate, sodium acetate, and ammonium chloride salts are introduced into the corresponding solutions. Explain the observed phenomenon.

9.4 HYDROLYSIS OF SALTS

Put a piece of indicator paper (a universal indicator) on a watch glass and wet it with a sodium carbonate solution. Note the change in the indicator colour, compare it with a reference, and determine the pH of the sodium carbonate solution. Perform similar experiments with aluminium and sodium chlorides. Use the pH values obtained to calculate the hydrogen ion concentrations in the studied solutions.

Explain why the equality of the hydrogen ion and hydroxyl ion concentrations is violated when certain salts are dissolved in water. Compare the values of the dissociation constants of water, acetic acid, carbonic acid, the bicarbonate ion, and aluminium hydroxide. How can the hydrolysis process be explained from the viewpoint of the law of mass action? In what cases is hydrolysis reversible and in what cases does it proceed virtually to the end?

Write the equations of the hydrolysis reactions of the studied salts in the molecular and net ionic forms. Define the degree of hydrolysis and the hydrolysis constant.

9.5 SOLUBILITY PRODUCT

Precipitation of Sparingly Soluble Salts. Pour 2-3 ml of barium chloride, strontium chloride, and calcium chloride solutions into three test tubes. Add a sodium sulphate solution to the first tube, a saturated calcium sulphate solution to the second one, and a saturated strontium sulphate solution to the third one. Write the equations of the chemical reactions in the molecular and net ionic forms.

Explain the formation of precipitates using the concept of the solubility product (see Appendix 1, Table 12). In what cases was no precipitate formed when the salts were poured together?

Dissolution of Sparingly Soluble Salts. Obtain precipitates of calcium carbonate and calcium oxalate in test tubes by reacting the relevant salts. Decant the solutions and pour an acetic acid solution onto the moist precipitates. What happens? Repeat the experiment, but use hydrochloric acid instead of the acetic acid. Write the equations of the chemical reactions in the molecular and net ionic forms. Explain the results obtained on the basis of the dissociation constants of the acids and the solubility product.

10 ELECTROCHEMICAL PROPERTIES OF SOLUTIONS

10.1 ELECTROCHEMICAL SERIES

Reaction of Metals with Salts. 1. Pour a small amount of a copper sulphate solution into two test tubes. Immerse an iron plate or nail into one of them and a piece of lead into the other.

2. Immerse an iron plate into a test tube containing a lead acetate solution.

Note the observed phenomena. Write the molecular and net ionic equations of the reactions occurring between the metals and the salts. Arrange the metals in a series according to their activity (the electrochemical series), writing down the values of their standard electrode potentials (see Appendix 1, Table 2). What place does hydrogen occupy in this series?

Reaction of Non-Metals with Salts. 1. Add 0.5 ml of petrol and several drops of chlorine water to each of potassium bromide and iodide solutions. Stir the solutions with a glass rod. Note the colour of the petrol layer. Write the equations of the reactions in the molecular and net ionic forms.

2. Add 0.5 ml of petrol and a few drops of bromine water to a potassium iodide solution. How can the change in the colour of the petrol solution be explained? Write the equation of the reaction.

3. Pour hydrogen sulphide water into three test tubes and treat it with chlorine, bromine, and iodine water. What is observed? Write the equations of the reactions. Arrange the non-metals in a series according to their activity.

Find the values of the standard oxidation-reduction potentials of the indicated systems (see Appendix 1, Table 21). Write the Nernst equation.

10.2 ELECTROLYSIS

Electrolysis of a Copper(II) Chloride Solution. Pour a 5% copper chloride solution into U-tube *3* (Fig. 52). Use carbon bars as electrodes. Fit small pieces of rubber tubes onto carbon electrodes *4* so that the ends of the electrodes protrude by 2 cm. Secure the electrodes with the aid of two stoppers (*do not close the tube tightly*). Connect the wires to a 10-20-V current source (or to an accumulator), and include rheostat *1* for 10-20 Ω and 2-3 A, and ammeter *2* in the circuit.

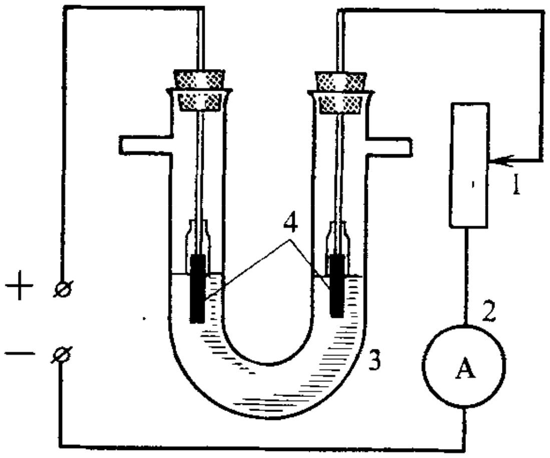


Fig. 52. Device for the electrolysis of a copper chloride solution

Immerse the electrodes into the solution up to the rubber tubes and switch on the current. The latter should be about 2 A. Carry on electrolysis for 5-10 min. Add two or three drops of a starch iodide solution to the tube arm containing the anode. What do you observe? What substances evolve at the electrodes? Write the equations of the reactions occurring at the electrodes. State Faraday's law. Define the electrochemical equivalent.

After completing work, wash the electrodes with a 10% nitric acid solution, and then with water.

Electrolysis of Sodium Sulphate Solution. Use the device of the preceding experiment. Pour a 5% sodium sulphate solution into the U-tube and add two drops of a neutral litmus solution to each arm of the tube. Switch on the current (it should be about 2 A). Observe the phenomena occurring at the electrodes. Write the equations of the corresponding reactions. What is known as the electrolyte decomposition voltage?

Preparation of Zinc by the Electrolysis of a Zinc Sulphate Solution. Pour a 1 *N* zinc sulphate solution into a 300-ml beaker and put a strip of aluminium foil 4 cm wide (cathode) into it. A carbon bar can be used as the anode. The current source must have a voltage of 10 V and provide a current of 1-1.5 A. Close the circuit. What happens? Continue electrolysis until a sufficient amount of zinc forms. Do not let the deposited metal come into contact with the other electrode. What substances are formed at the electrodes? Write the equations of the reactions.

Electrolytic Refining of Copper. Immerse a carbon cathode and an anode cut out from a strip of "crude" copper into a 300-ml beaker. Pour a 20% sulphuric acid solution into the beaker. The current

source (accumulator) must have a voltage of 2-10 V. Begin electrolysis at a cathode density of 6 A/dm^2. When the solution acquires a noticeable light blue colour (why?), lower the cathode current density to 0.5 A/dm^2. Continue electrolysis for 10-15 min. Explain the processes occurring at the electrodes.

Anode Oxidation of Lead. Suspend two lead plates to be used as electrodes in a beaker and pour in a 25% sulphuric acid solution. Use a 10-V current source. Switch on the current and continue electrolysis up to a noticeable change in the colour of one of the electrodes. What is it due to? Write the molecular and net ionic equations of the occurring reactions.

11 HALOGENS. PREPARATION AND PROPERTIES

Indicate the position of the halogens in Mendeleev's periodic table, their electron configurations, the size of their atoms, and the exhibited oxidation states. Write the electron configurations of the halogen molecules. How does the binding energy change in them?

11.1 CHLORINE

Chlorine is a poisonous greenish-yellow gas. The inhalation of small amounts of chlorine causes coughing. When large amounts of chlorine are inhaled, major affection of the respiratory tracts is possible.

Perform all work with chlorine in a fume cupboard in the presence of your instructor! A person poisoned by chlorine must immediately be taken out into the fresh air, and the following measures taken: let him (or her) smell a dilute solution of ammonia or ethanol and make cold compresses on his chest and neck. In case of serious poisoning, call a doctor.

PREPARATION METHODS

Preparation of Chlorine from Hydrochloric Acid by the Action of Various Oxidizing Agents. 1. Spill a small amount of manganese dioxide into a test tube and add concentrated hydrochloric acid. Carefully smell the chlorine by directing a stream of it toward your face with a wave of your hand. Write the equation of the reaction.

2. Put two or three potassium permanganate crystals in a test tube and secure it in a stand. Carefully add several drops of concentrated hydrochloric acid. What do you observe? Write the equation of the reaction.

3. Spill some finely triturated potassium dichromate onto the bottom of a test tube and pour concentrated hydrochloric acid over

it. Slightly heat the mixture. Comment on your observations. Write the equation of the reaction.

4. Put some chlorinated lime into a test tube and pour a 20% hydrochloric acid solution over it. Write the equation of the reaction.

Preparation of Chlorine from Sodium Chloride. 1. Put a small amount of a mixture of sodium chloride and manganese dioxide into a test tube and carefully add a few drops of a 96% sulphuric acid solution from a pipette. Slightly heat the mixture. What is observed? Write the equation of the reaction.

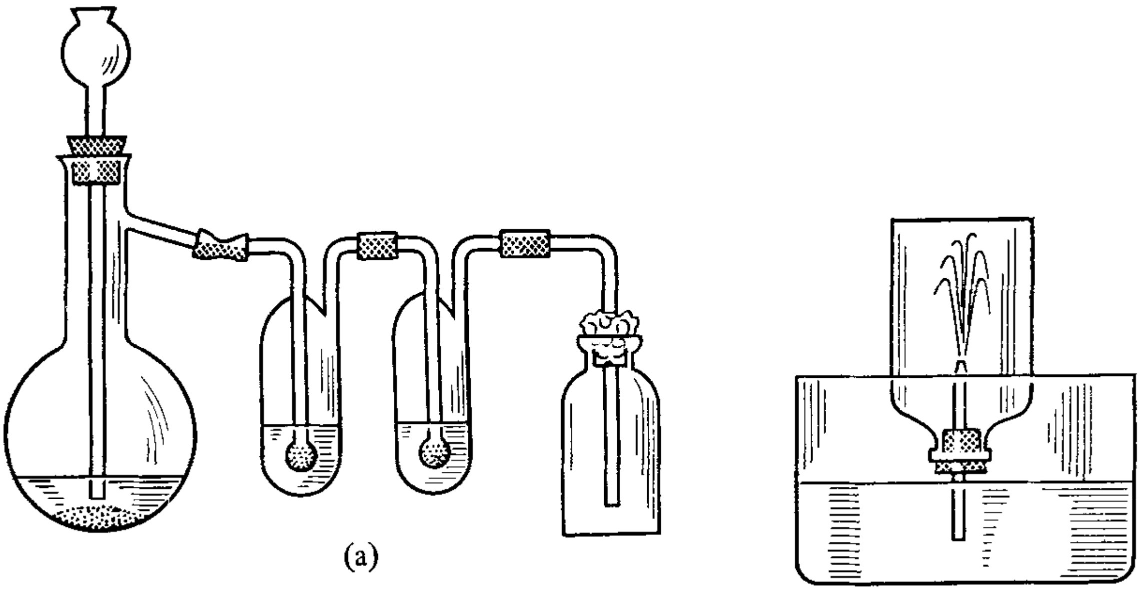
2. *The experiment is prepared by one student and demonstrated to the class.* Assemble a device for electrolysis (see Fig. 52). Include rheostat *1* for 10-20 Ω and ammeter *2* for 2-3 A in the circuit. Pour a saturated sodium chloride solution coloured with a neutral litmus solution into U-tube *3*. Immerse carbon electrodes *4* (by one-third) into the solution. Connect the ends of the conductors to a direct-current source (an accumulator) and pass a current of about 2 A through the solution. What is observed? Explain the change in the colour of the indicator solution. Write the equations of the reactions proceeding at the electrodes.

What chlorine compounds are encountered in nature? How is chlorine produced in the industry?

PREPARATION AND STUDYING OF PROPERTIES

Chlorine can be prepared by reacting hydrochloric acid with manganese dioxide or with potassium permanganate.

Preparation of Chlorine by Oxidizing Hydrochloric Acid with Manganese Dioxide. Assemble an apparatus (Fig. 53). Pour water



(a) (b)

Fig. 53. Apparatus for preparing chlorine and hydrogen chloride

into the first wash bottle (why?) and concentrated sulphuric acid into the second one (why?). Spill 20 g of manganese dioxide into the 250-ml flask and pour in concentrated hydrochloric acid until it covers the dioxide and the end of the funnel stem. When the gas evolves slowly, slightly heat the reaction flask.

Fill five 25-50-ml bottles with chlorine and cover them with glass plates. When filling the bottles with chlorine, cover their mouths with glass plates or sheets of paper. Put a white screen (a sheet of paper) behind the bottles to observe the colour of the chlorine. Test its properties.

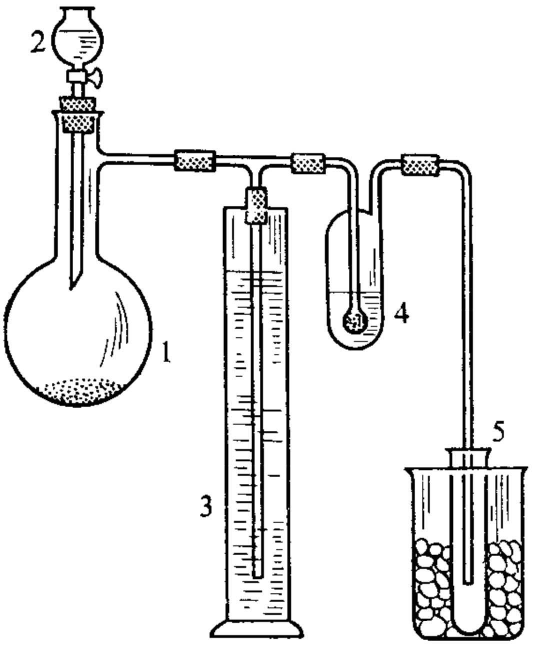


Fig. 54. Apparatus for preparing chlorine by reacting hydrochloric acid with potassium permanganate. Liquefaction of the chlorine

Preparation of Chlorine by Oxidizing Hydrochloric Acid with Potassium Permanganate. Liquefaction of the Chlorine. Assemble an apparatus as shown in Fig. 54. Spill 10-15 g of potassium permanganate into flask *1*. Pour a 37% hydrochloric acid solution into dropping funnel *2*, a saturated sodium chloride solution into cylinder *3*, and a little concentrated sulphuric acid into wash bottle *4*. Put the end of the gas-discharge tube of the apparatus into test tube *5* cooled outside by solid carbon dioxide (dry ice) wetted with acetone. What is the boiling point of chlorine?

What is the purpose of the cylinder with the saturated sodium chloride solution? Why is no wash bottle with water used in the given apparatus? Will the liquid chlorine be contaminated with hydrogen chloride?

By adding hydrochloric acid dropwise from funnel *2*, obtain a uniform stream of chlorine. After 2-3 ml of liquid chlorine gather in the receiver, disconnect the apparatus from wash bottle *4*. Pour the obtained liquid chlorine into five bottles and cover them with glass plates.

Reaction of Chlorine with Metals. 1. Put a little of antimony powder on a sheet of paper, open one of the bottles with chlorine and gradually spill the antimony into it. What happens? Write the equation of the reaction.

2. Take a strip of copper foil or a bundle of thin copper wires with pincers, heat it in the flame of a burner, and rapidly introduce it into a bottle with chlorine. What do you observe? Write the equation of the reaction.

Reaction of Chlorine with Non-Metals. 1. Put several grains of red phosphorus into a spoon for burning, ignite it, and introduce it into a bottle with chlorine. What occurs? Write the equation of the reaction.

Under what conditions can phosphorus (antimony) trichloride and pentachloride form when phosphorus (antimony) burns in chlorine? By what features can we distinguish them from each other?

2. Take two test tubes. Fill one of them with chlorine, and the other with hydrogen from a Kipp gas generator. Close the mouths of the tubes with your fingers and connect them so that the tube with the chlorine is on top. Separate the tubes and rapidly introduce their mouths into a flame. What happens? Write the equation of the reaction.

Reaction of Chlorine with Compounds. 1. Take a strip of filter paper, wet it with several drops of freshly distilled turpentine, and introduce it, using pincers, into a bottle with chlorine. What is observed? Write the equation of the reaction.

2. Secure a candle stub on a spoon for burning, ignite the candle, and carefully introduce it into a bottle with chlorine. What do you observe? What products form as a result of the reaction?

Chlorine Water and Its Properties. 1. Saturate 5-10 ml of distilled water with chlorine. Note the colour and odour (*carefully!*) of the solution obtained. What substances are present in chlorine water? Write the equation of the reaction and its equilibrium constant. Test how the obtained chlorine water affects an indigo solution and coloured fabric. What is observed? What substance has a bleaching effect?

2. Pour 2-3 ml of chlorine water into a test tube and add a sodium hydroxide solution dropwise. How can the vanishing of the colour and odour of the chlorine water be explained? How does the alkali shift equilibrium in the reaction between chlorine and water? State le Chatelier's principle.

Add a dilute solution of sulphuric acid to the test tube up to an acid reaction. Did the odour of the solution change? Write the equation of the reaction. Explain the results obtained. How can a hypochlorous acid solution be prepared? What kinds of transformations are typical of hypochlorous acid? What conditions facilitate each kind of transformation?

11.2 BROMINE

Perform all work with bromine in a fume cupboard, wear eye protection or a mask and rubber gloves.

Bromine is a heavy reddish-brown liquid. Bromine vapour has the same colour. It affects the respiratory tracts. If a student has accidentally inhaled bromine vapour, take him (her) into the fresh air; it is

prudent to let him also inhale ammonia vapour (a 2% aqueous solution). If liquid bromine gets onto your skin, rapidly wash the affected area with ethanol, then with a large amount of water and a 2% solution of sodium bicarbonate.

PREPARATION

Preparation of Bromine by the Oxidation of Hydrobromic Acid. Assemble the setup shown in Fig. 55. Spill about 1.5 g of manganese dioxide into test tube *1* and pour in 5 ml of concentrated hydrobromic acid. Close test tube *1* with a stopper containing a gas-discharge tube, and lower its end into dry test tube *2* cooled with ice. Close the mouth of tube *2* with cotton wool and, by slightly heating the reaction mixture, gather the evolving bromine. Write the equation of the reaction. Use the obtained bromine for later experiments.

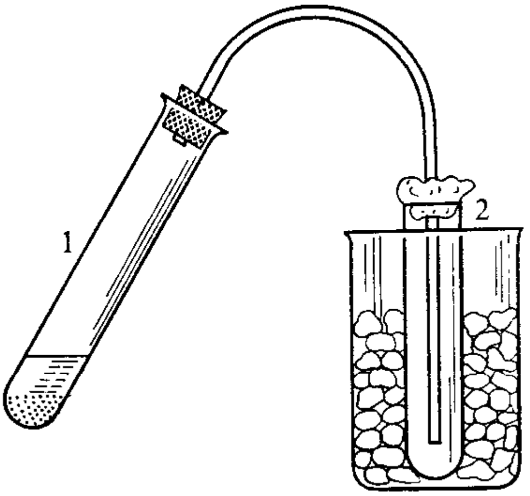


Fig. 55. Setup for preparing bromine

Preparation of Bromine by Displacing It from Its Salts. Pour 2-3 ml of a saturated potassium bromide solution into a test tube and pass a strong stream of chlorine through it. What occurs? Distil off the prepared bromine into a receiver test tube (see Fig. 55). Write the equation of the reaction. Can chlorine and iodine be prepared in this way?

PROPERTIES

Perform experiments with liquid bromine in the presence of your instructor.

Put a test tube stand with five dry test tubes in a fume cupboard. Using a small funnel, pour 0.3-0.5 ml of bromine into each tube and perform the following experiments.

1. Put one test tube with bromine into a beaker with a cooling mixture (ice and sodium chloride) whose temperature should not exceed —10 °C. What is the freezing point of bromine?

2. Fasten a test tube with bromine in a clamp of the stand and throw a narrow strip of aluminium foil into it. If no reaction begins after a minute, put a beaker with warm water (about 40 °C) under the bottom of the test tube. What happens? Write the equation of the reaction.

3. Introduce a heated strip of copper foil into a test tube filled with bromine and fastened in a stand clamp. What do you observe? Write the equation of the reaction.

4. Introduce several grains of red phosphorus with a spatula into the fourth tube with bromine. Write the equation of the reaction.

5. Add 3-5 ml of water into a test tube with bromine and stir its contents with a glass rod. What is observed? Is the solubility of bromine in water high? What is called bromine water? Add a few drops of a saturated potassium bromide solution to this tube containing bromine water and stir its contents. Explain what occurs.

6. Pour 2-3 ml of bromine water into a test tube and add a sodium hydroxide solution. How can the change in the colour of the solution be explained? Write the equation of the reaction.

7. Pour several drops of bromine water into a test tube, dilute it with 5 ml of distilled water, and add 5-10 drops of chloroform. Thoroughly stir the contents of the test tube. Explain the observed phenomenon. Perform a similar experiment with other organic solvents (petrol, benzene, carbon disulphide, carbon tetrachloride).

Note the change in the colour of the organic layer.

11.3 IODINE

Iodine is a violet-black crystalline substance. Iodine vapour irritates the respiratory tracts and the mucous membrane. If poisoned by iodine vapour, inhale vapour of a 2% aqueous solution of ammonia.

PREPARATION

1. Weigh 0.5 g each of potassium iodide and manganese dioxide, place the substances into a crucible, and mix them with a glass rod. Put the crucible with the mixture on a porcelain triangle, pour in 3-4 drops of concentrated sulphuric acid, and cover the crucible with a small round-bottomed flask filled with cold water. Fasten the flask in a clamp of a stand. Slightly heat the crucible during several minutes. What do you observe? Write the equation of the reaction. Collect the iodine obtained in a weighing bottle and weigh it. Calculate the yield in per cent. Hand in the substance obtained to the laboratory assistant.

2. Pour 5 ml of a saturated potassium iodide solution into a test tube. Pass a stream of chlorine through the solution. What substance evolves? Filter the substance on a smooth filter and dry it in the air. What impurity will the iodine contain? How can it be purified?

PROPERTIES

1. Put several crystals of the obtained dry iodine and an aluminium powder into a small porcelain bowl and carefully mix them (*perform the experiment in a fume cupboard!*). Introduce a drop of water into the prepared mixture with the aid of a long tube or rod. What is observed? What role is played by the water in the given experiment? Write the equation of the reaction.

2. Pour water into two test tubes and lower one crystal of the iodine prepared in the preceding experiments into each of them. Vigorously shake the contents of the tubes. What is the solubility of iodine in water? Write the equation of the reaction of iodine with water.

Leave one test tube for comparison, add a saturated potassium iodide solution to the second tube, and vigorously shake it. What happens? The formation of what substance explains the increase in the solubility of iodine? Write the equation of the reaction.

3. Add a 1 *N* alkali solution to 2-3 ml of iodine water until the colour of the solution vanishes. Acidify the solution with sulphuric acid. What is observed? Explain the occurring phenomena. Write the equations of the reactions.

4. Pour 2-3 ml of iodine water into each of several test tubes and add 2-3 drops of an organic solvent to each of them (benzene, chloroform, petrol, carbon disulphide, carbon tetrachloride). Shake the contents of the tubes and note the colour of the organic solvent layer. What is the essence of the distribution law?

11.4 FLUORINE

1. How is fluorine prepared?

2. How does fluorine react with the hydrogen compounds of other elements, for example, with water, hydrogen sulphide, and ammonia?

3. How does the activity of the halogens change in the series from fluorine to iodine? How can this be explained?

11.5 HYDROGEN COMPOUNDS OF THE HALOGENS

(*Perform the experiments in a fume cupboard!*)

Reaction of Sodium Chloride, Sodium Bromide, and Potassium Iodide with Concentrated Sulphuric Acid. Put three test tubes on a stand. Put a little sodium chloride in the first of them, sodium bromide in the second, and potassium iodide in the third. Pour several drops of concentrated sulphuric acid into each tube (*handle the acid with a pipette or tube having a rubber bulb!*). What do you observe? What impurities do hydrogen bromide and iodide prepared in this way contain? Write the equations of the reactions.

Which of the hydrogen halides is the strongest reducing agent? Which hydrogen halides can be prepared by the action of concentrated sulphuric acid on the relevant halide?

Reaction of Sodium Bromide and Potassium Iodide with Concentrated Orthophosphoric Acid. Put a small amount of sodium bromide in one test tube and of potassium iodide into another one. Add a 60% orthophosphoric acid solution to both tubes. What gases evolve from the test tubes? Write the equations of the reactions and explain their course.

HYDROGEN CHLORIDE

Preparation. (*Perform the experiment in a fume cupboard*!) Assemble an apparatus as shown in Fig. 53*a*, substituting a U-tube for the wash bottles. Place 10-15 g of sodium chloride into the reaction flask, and anhydrous calcium chloride in the U-tube. Pour 20-25 ml of a 70% sulphuric acid solution into the flask via the funnel, and see that the end of the funnel tube is submerged in the liquid. Fill a dry thick-walled 25-50-ml bottle with the evolving hydrogen chloride. How can you tell that the bottle is filled?

Dissolution in Water. Close the bottle containing hydrogen chloride with a stopper provided with a capillary facing inward. Invert the bottle with the gas and immerse its neck in a bath with water (see Fig. 53*b*). Explain what occurs.

What is the solubility of hydrogen chloride in water? What is the composition of an azeotropic mixture of hydrochloric acid with water? What is called an azeotropic mixture of liquids and how does it differ from the pure liquids? Why are dry sodium chloride and concentrated sulphuric acid taken when preparing hydrogen chloride? How is hydrochloric acid produced in the industry? What is the percent concentration of commercial hydrochloric acid?

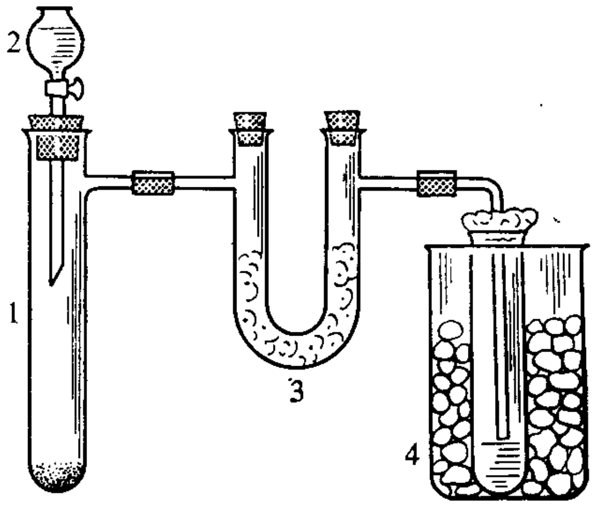


Fig. 56. Apparatus for preparing hydrogen bromide

HYDROGEN BROMIDE

Preparation of Hydrobromic Acid. (*Perform the experiment in a fume cupboard*!) Assemble an apparatus as shown in Fig. 56. Put 1 g of red phosphorus wetted with two drops of water into test tube *1*. Pour 3-5 ml of bromine into dropping funnel *2*. Place a wad of glass wool mixed with red phosphorus into the bottom part of U-tube *3*

(why?). Pour 3 ml of water into test tube *4* used as a receiver and lower it into a beaker with ice. See that the gas-discharge tube is not submerged into the water in the receiver (why?), but that its mouth is very close to the surface of the water. Slowly, dropwise, pour the bromine into the phosphorus, seeing that the bromine has time to react. When the reaction between the bormine and the phosphorus terminates, heat the test tube for another 3-5 min, and then remove the receiver. Determine the concentration of the prepared acid.

Properties of Hydrobromic Acid. 1. See how the prepared hydrobromic acid acts on a metal (magnesium or zinc) and on calcium carbonate.

Add 1-2 drops of a silver nitrate solution to 1 ml of a hydrobromic acid. What do you observe? Write the equations of the reactions for all the processes occurring in the given experiment.

HYDROGEN IODIDE

Preparation of Hydroiodic Acid. (*Perform the experiment in a fume cupboard!*) Assemble an apparatus as shown in Fig. 56. Put 2 g of iodine and 0.5 g of red phosphorus into test tube *1*. Pour 3-5 ml of water into test tube *4*. The opening of the offtake tube must be as close as possible to the surface of the water in the receiver. Why must it not be submerged into the water?

Carefully release one drop of water from the dropping funnel and see what happens. After the vigorous reaction terminates, again release a drop of water from the funnel. When all the water is introduced into test tube *1*, heat the test tube. What gas evolves? Does it dissolve well in water? Write the equations of the reactions.

Properties of Hydroiodic Acid. 1. Test the obtained hydroiodic acid solution with litmus. Study its relation to metals (zinc, magnesium).

2. Pour a hydroiodic acid solution into three test tubes. Add solutions of sodium acetate and lead acetate to the first tube, of silver nitrate (one or two drops) to the second one, and put a small piece of marble into the third tube. Write the equations of the reactions for all the processes occurring in the given experiment.

HYDROGEN FLUORIDE

Perform all work with gaseous hydrogen fluoride, and also with hydrofluoric acid in a fume cupboard! When pouring hydrofluoric acid into a vessel, wear rubber gloves and eye protection or a mask. See that no drops of the acid get onto your skin. Thoroughly wash an affected area with water and put cotton wool wetted with a 10% calcium chloride solution on it.

Preparation of Hydrofluoric Acid. Put 5 g of fluorite and 1 g of gypsum into a Teflon (polytetrafluoroethylene), lead, or copper test tube (why is gypsum added?). Pour 5 ml of a 96 % sulphuric acid solution over the mixture, tightly close the test tube with a rubber stopper provided with a Teflon, lead, or copper gas-discharge tube. Lower the end of this tube into a Teflon, lead, copper, or paraffin-coated glass beaker containing 10 ml of water so that it only slightly touches the surface of the water (why?). Put an asbestos sheet between the beaker and the Teflon test tube. To speed up the reaction, it is recommended to immerse the Teflon test tube into a beaker with hot water. Why must the test tube not be heated directly by the flame of a burner?

Properties of Hydrofluoric Acid. 1. See how the prepared hydrofluoric acid solution acts on litmus and zinc.

2. Pour a calcium chloride solution into 1 ml of a hydrofluoric acid one. What do you observe? Write the equations of the reactions.

The fluorides of what metals are soluble in water? How can you explain the low degree of dissociation of hydrofluoric acid? What is the percent concentration of hydrogen fluoride in its azeotropic mixture with water and in commercial hydrofluoric acid?

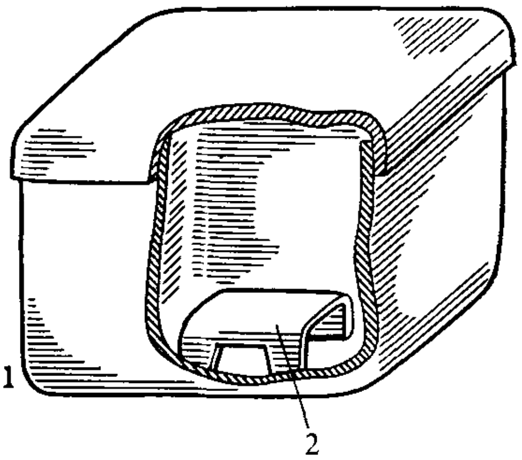


Fig. 57. Device for etching glass with hydrogen fluoride

Etching of Glass with Hydrofluoric Acid. Cover a glass plate with a layer of paraffin. To do this, lower it into paraffin melted in a porcelain bowl and immediately extract it. Make an inscription with a penknife on the paraffin-coated surface so as to uncover the surface of the glass. Make a small paraffin barrier at the edges of the inscription. Pour a 10 % hydrofluoric acid solution onto the paraffin-coated plate and let it stand in a fume cupboard. After one or two hours, wash the solution off the plate and remove the paraffin. What happened to the glass? Write the equations of the reactions.

Etching of Glass with Gaseous Hydrogen Fluoride. (The experiment is performed by one student and demonstrated to the class.)

Put a mixture of 5 g of calcium fluoride and 1 g of calcium sulphate into lead vessel *1* (Fig. 57). Put a paraffin-coated glass plate with an inscription onto lead support *2* with the inscription downward. Pour 5 ml of concentrated sulphuric acid onto the calcium fluoride and cover the vessel with its lead lid. In an hour, extract the plate with tongs, thoroughly wash it with water, and remove the paraffin. How does the surface of glass etched with gaseous hydrogen fluoride

differ from that etched with a solution of hydrogen fluoride? How can the difference in etching be explained?

How do the polarity, the Gibbs function, and the binding energy change in hydrogen halide molecules? How do the reducing properties and the strength of the hydrogen halide acids change?

11.6 OXYGEN COMPOUNDS OF THE HALOGENS

CHLORINATED LIME (BLEACHING POWDER)

Preparation. (*Perform the experiment in a fume cupboard!*) Add 10-15 ml of water to 2 g of pure slaked lime (calcium hydroxide) and stir thoroughly. Put the mixture in a small beaker cooled with ice (why is cooling needed?) and pass chlorine purified from hydrogen chloride (how can this be done?) through it during 10-20 min. Write the equation of the reaction.

Properties. 1. Treat a part of the prepared substance with 10 ml of water and filter off the undissolved matter. Take a small amount of the solution and see how it acts on indigo and coloured fabric. Explain what you observe.

Can carbonic acid displace hypochlorous acid from a solution of its salt? Compare the values of the dissociation constants of carbonic and hypochlorous acids (see Appendix 1, Table 9).

2. Add a solution of 1 *N* sulphuric acid to a part of the prepared chlorinated lime solution until the reaction is acid and carefully smell the product. Write the equation of the reaction. What happens to chlorinated lime when its concentrated solution is heated?

How does the strength of the acids change in the series including hypochlorous, hypobromous, and hypoiodous acids? What ions do solutions of these acids contain? How do the stability and oxidizing effect of the acids change in this series? Explain the observed laws.

POTASSIUM CHLORATE

Preparation. (*Perform the experiment in a fume cupboard, wear eye protection!*) Pour 15-20 ml of a 50% potassium hydroxide solution into a beaker, heat it almost to boiling, and pass a stream of chlorine through it. Connect a small funnel to the outlet opening of the gas-discharge tube. The wide part of the funnel should contact the heated potassium hydroxide solution. See that the opening of the gas-discharge tube is not clogged with the formed salts. Write the equation of the reaction. How can you see that the reaction has terminated? Filter off the formed crystals on a funnel with a filtering bottom, and then recrystallize the salt from a minimum amount of hot water. Examine the shape of the crystals under a microscope. How can one prove that the prepared substance is potassium chlorate?

Properties. (*Perform the experiment in a fume cupboard!*) **1.** Put several potassium chlorate crystals into a small porcelain bowl and carefully wet them with 3-4 drops of a 96% sulphuric acid solution. What is observed? Perform a similar experiment with concentrated hydrochloric acid. What is observed in this case? Write the equations of the reactions. What products form when potassium chlorate reacts with oxalic acid?

2. Weigh 0.5 g of finely crystalline potassium chlorate and mix it with an equal amount of powdered sugar, using a rod (*be careful!*). Pour out the mixture onto the lid of a crucible and wet it with two or three drops of concentrated sulphuric acid. What occurs? What properties of potassium chlorate do the above experiments indicate?

IODIC ACID

Prepare a solution of iodic acid (see p. 109) and pour it into two test tubes. Pour a potassium iodide solution into one tube. What substance evolves? Pour an iron(II) sulphate solution into the other tube. What do you observe? Write the equations of the reactions. What properties of iodic acid do the above experiments indicate? Write the formulas of the iodine oxyacids. What oxygen compounds of iodine are known? How are they prepared?

11.7 COMPARISON OF OXIDIZING PROPERTIES OF THE HALOGENS

1. Pour 1 ml of a bromine water solution into a test tube, the same amount of an iodine water solution into another tube, dilute the solutions with 2-3 ml of water, introduce several drops of an organic solvent such as carbon tetrachloride, chloroform, or benzene into each of them, and vigorously shake them. While adding chlorine water dropwise to both test tubes and vigorously shaking them, watch the change in the colour of the organic solvent layer. Write the equations of the reactions.

2. Pour a drop each of potassium iodide and bromide and 3-5 drops of an organic solvent into a test tube. Add chlorine water dropwise, vigorously shake the contents, and watch how the colour of the solvent layer changes. Write the equations of the reactions.

3. Prepare a little of a bromic acid solution. To do this, mix 2-3 drops of a saturated potassium bromate solution with 1-2 ml of a dilute sulphuric acid solution. Throw a minute iodine crystal into the solution, mix the test tube contents several times, decant the solution, and add several drops of an organic solvent to it. What is observed? Write the equations of the reactions. Will bromine displace iodine from iodic acid?

Arrange the halogens in a series according to their ability of displacing one another from solutions of the hydrogen halides and their salts, and also from oxygen compounds, and explain this phenomenon proceeding from the values of the standard oxidation-reduction potentials. Which of the halogens form a larger number of oxygen compounds? What is the essence of the phenomenon of secondary periodicity observed in the group of halogens?

SUPPLEMENTARY EXPERIMENTS AND SYNTHESES

1. Preparation of Chlorine by Reacting Oxygen with Hydrogen Chloride. Assemble an apparatus as shown in Fig. 58, pour 3-5 ml of a 96% sulphuric acid solution into each of wash bottles *1* and *2*,

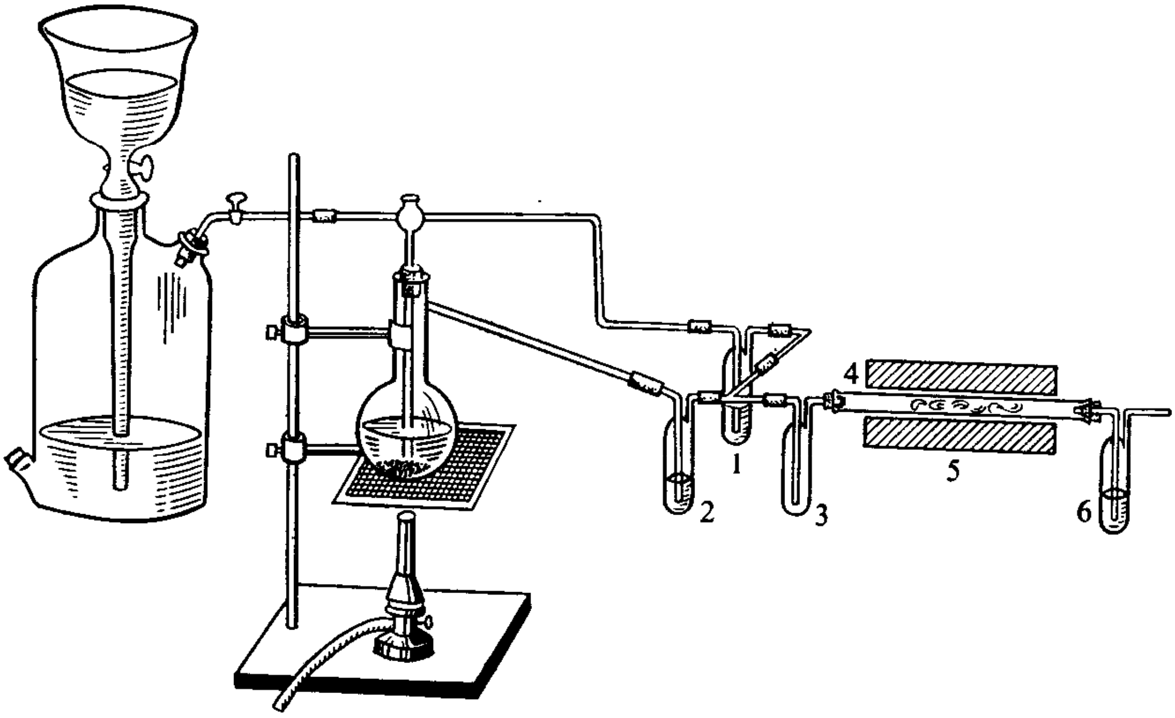


Fig. 58. Apparatus for preparing chlorine by reacting hydrogen chloride with oxygen

making sure that the openings for the discharge of the gases are submerged in the acid, and leave wash bottle *3* empty (it is intended for mixing the gases). Treat asbestos with a boiling saturated copper(II) chloride solution and dry it in a drying cabinet. Place the asbestos prepared in this way into quartz tube *4* accommodated in tubular furnace *5*. Pour an indigo solution into wash bottle *6*. Connect a gas meter with oxygen to wash bottle *1* and an apparatus for preparing hydrogen chloride to wash bottle *2*.

Heat the furnace to a temperature of 450-500 °C (*use a thermocouple!*) Adjust the rate of feeding the gases into wash bottle *3* in accor-

dance with the stoichiometric ratio of oxygen and hydrogen chloride needed for the complete proceeding of the reaction.

Why must the temperature not be raised above 600 °C? Write the equation of the expected reaction. How is the change in the colour of the indigo explained?

2. Preparation of Purified Iodine. Dissolve 32 g of potassium iodide in 100 ml of water and 25 g of copper sulphate pentahydrate in 80 ml of water. Pour the solutions together into a 200-ml glass beaker and let the solution settle. Separate the precipitate from the

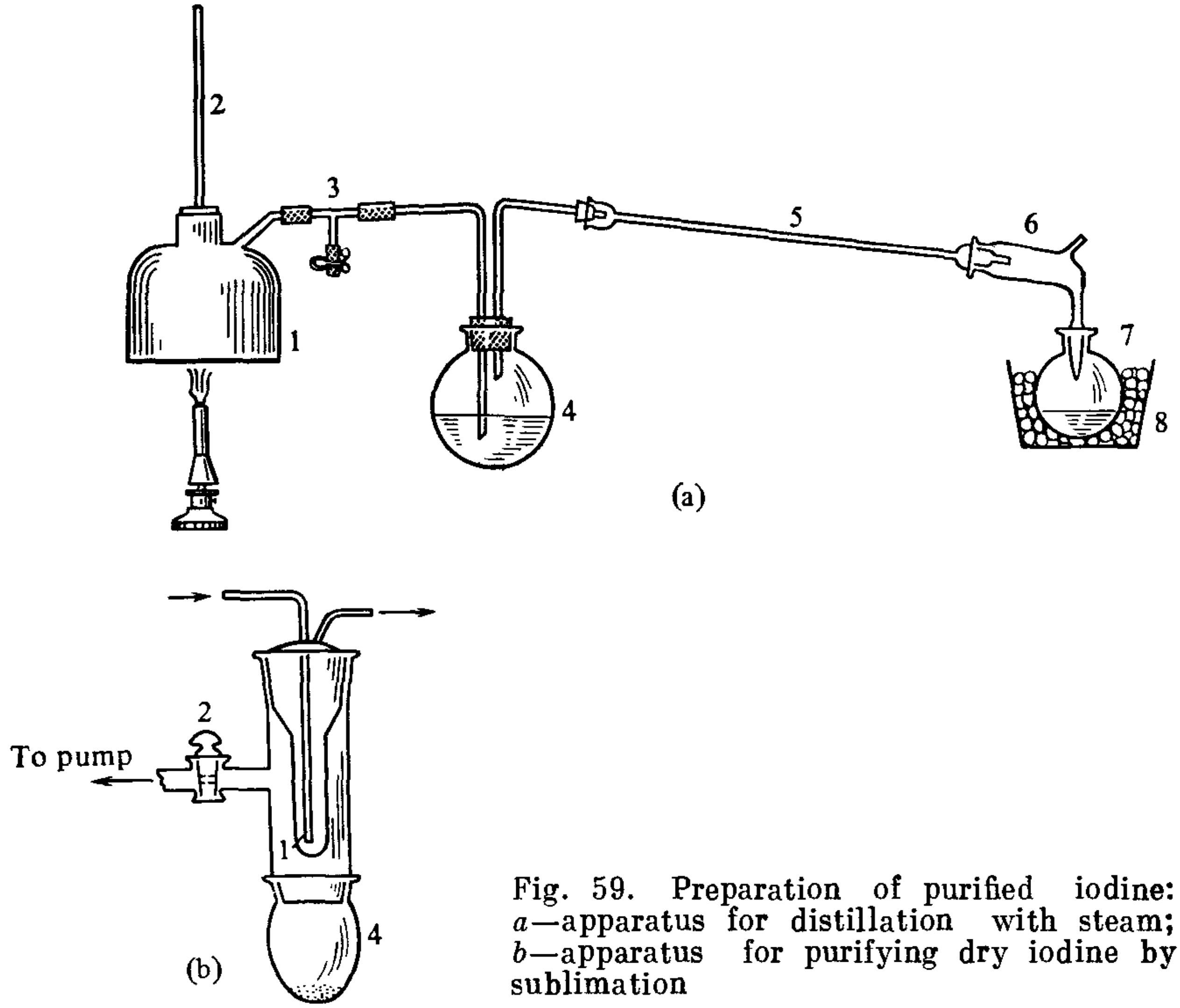


Fig. 59. Preparation of purified iodine: *a*—apparatus for distillation with steam; *b*—apparatus for purifying dry iodine by sublimation

liquid phase by decantation. Wash the precipitate with two 20-ml portions of a 20% potassium iodide solution. Combine all the solutions.

Assemble an apparatus for distillation with steam (Fig. 59*a*). Transfer the aqueous solution of iodine into flask *4*. Distil off the iodine. For this purpose, open the clamp on tee-piece *3* and heat the water in steam boiler *1* until it boils. Next regulate the rate of steam flow with the aid of the clamp and carefully heat flask *4*. After the main part of the iodine gathers in glass tube *5*, open the clamp and stop heating steam boiler *1* and flask *4*.

Remove the iodine crystals from tube *5*. Transfer them onto a glass plate, dry them with filter paper, and then put them in a desiccator over a concentrated sulphuric acid solution overnight.

Perform final purification of the iodine in the apparatus shown in Fig. 59*b*. Put the iodine in vessel *4*. Cool it with liquid nitrogen. Connect the apparatus to a fore pump. Evacuate the apparatus with cock *2* open (40 min), then close the cock, fill tube *1* with cold water, remove the liquid nitrogen so that vessel *4* acquires room temperature, and carefully heat it with the flame of a burner. When sublimation of the iodine is completed, cool the apparatus, carefully open cock *2*,

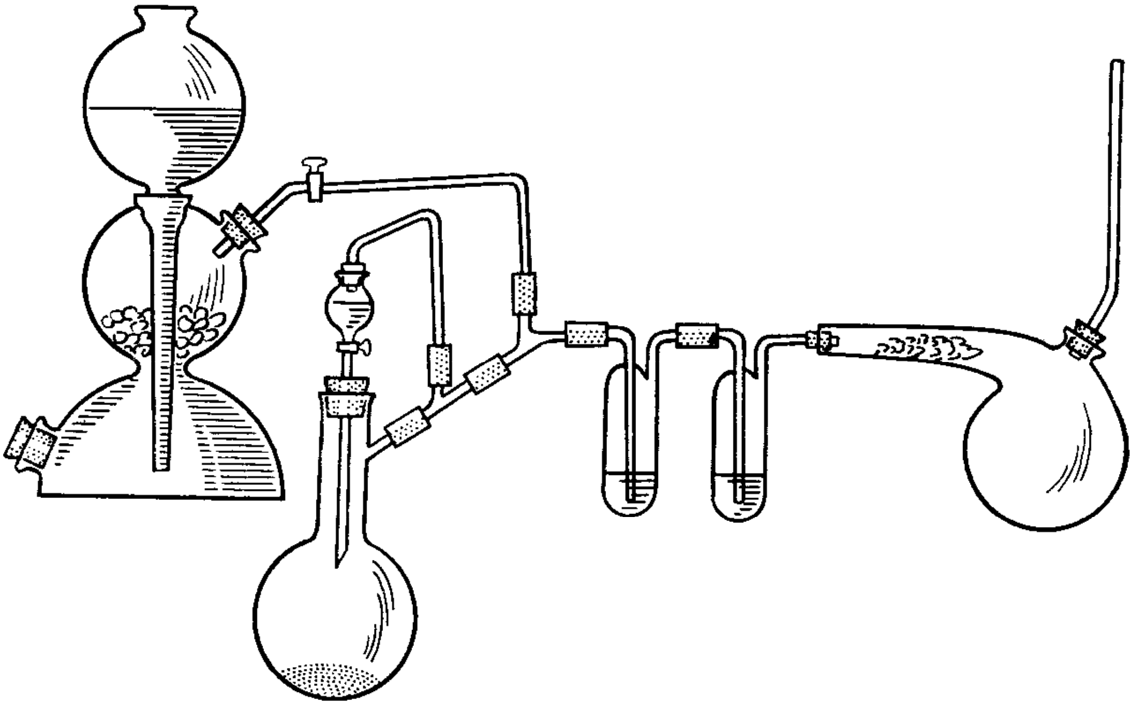


Fig. 60. Apparatus for preparing iron(III) chloride

and eliminate the vacuum. Extract tube *1* with iodine crystals deposited on its outer side from the apparatus and transfer the crystals into a jar with a ground glass stopper. Calculate the yield in per cent.

3. Preparation of Iron(III) Chloride. Assemble an apparatus for preparing dry chlorine (Fig. 60). Connect a Kipp gas generator with carbon dioxide via a tee-piece to the flask for preparing chlorine, and connect a retort to the wash bottles. (The retort can be replaced with a refractory glass tube.) Put 0.5 g of iron wire or shavings into the neck of the retort. Dry the apparatus and heat the iron wire in a stream of dry carbon dioxide with slight heating of the retort neck with a burner during 15-20 min. Stop the carbon dioxide stream, fill the apparatus with dry chlorine, and carefully heat the retort neck with the flame of a burner. Next, continuing to pass chlorine through the apparatus, heat the spot where the iron is more strongly. What is observed? Remove the burner if the wire becomes very hot.

When the reaction terminates, cool the retort in a chlorine stream, then displace the chlorine with a stream of dry carbon dioxide. Rapidly disconnect the retort from the wash bottles and remove the remaining unreacted metallic iron through its neck. Pour out the iron chloride through the tubulature of the retort into a preliminarily weighed dry test tube drawn out at its middle. Immediately seal the tube (*wear eye protection!*) and weigh it. Write the equation of the reaction. Calculate the yield in per cent.

Pour a little water into the retort with the residual iron chloride and immerse litmus paper into the solution. Explain what happens. Write the equation of the reaction.

4. Preparation of Nickel, Cobalt, or Chromium Chloride. When working with chlorine for a long period, prepare it by reacting con-

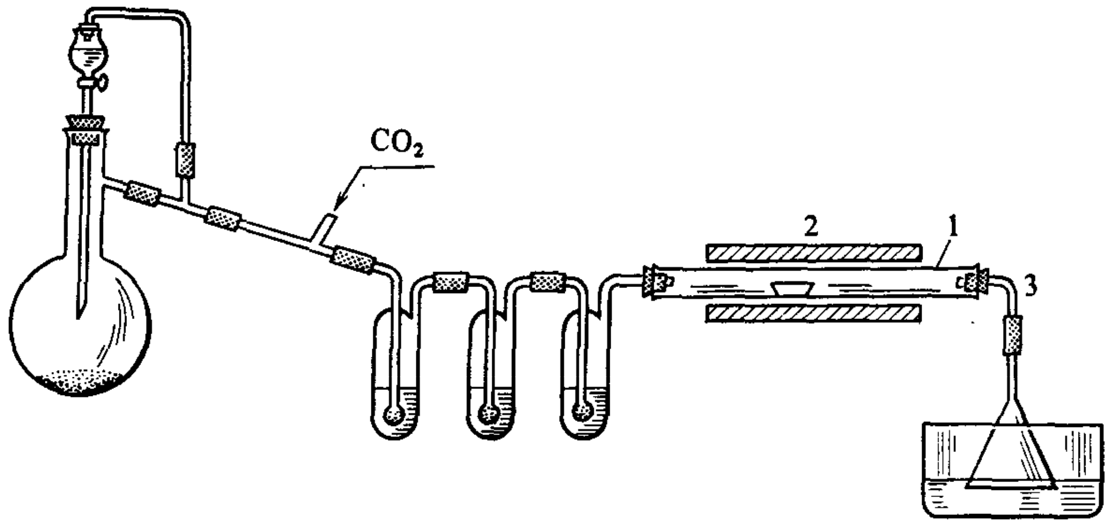


Fig. 61. Apparatus for preparing metal (nickel, cobalt, chromium) chlorides

centrated hydrochloric acid with potassium permanganate. Assemble an apparatus for preparing dry chlorine (Fig. 61). Leave the first wash bottle connected to the reaction flask empty or fill it with water. Why? Connect a Kipp gas generator with carbon dioxide to the system via a tee-piece. Connect the apparatus to quartz (or porcelain) tube *1* placed in tubular furnace *2*. Close the outlet opening of the tube with a stopper provided with bent tube *3* ending in a funnel. A solution of what substance must be poured into crystallizer *4* for absorbing the excess chlorine?

Spill 0.5 g of powdered metallic nickel (cobalt or chromium) into a boat and place it in the middle part of the quartz tube. Switch on the furnace. Dry the system with a stream of dry carbon dioxide during 30-40 min at 150-200 °C (*use a thermocouple*). Stop the carbon dioxide stream and fill the apparatus with dry chlorine. How can one tell that the apparatus is filled with chlorine? Raise the furnace temperature to 700-750 °C. (When synthesizing chromium chloride,

the furnace temperature must be at least 750 °C.) Perform chlorination during one hour, keeping the chlorine stream sufficiently intensive. *The chlorides of the indicated metals can sublime, therefore see that the outlet opening of the tube does not get clogged with the reaction products.* Switch off the furnace and let the tube cool in a chlorine atmosphere.

After cooling the tube, displace the chlorine with a stream of dry carbon dioxide. Transfer the preparation into a preliminarily weighed drawn out test tube (i.e. a tube with one end drawn out to a narrower diameter) and seal it (*wear eye protection!*). Calculate the yield in per cent. What is the colour and composition of the prepared substance?

5. Preparation of Ammonium Iodide. Put 10 g of the sublimed iodine and pour 50 ml of water into a 250-ml beaker. Simultaneously pour a 20% ammonia solution (40 ml) and a concentrated solution (30%) of hydrogen peroxide into the mixture from two dropping funnels. Stir the solutions with a mechanical mixer. Add the ammonia and hydrogen peroxide solutions until the colour vanishes completely; the latter should not reappear when the mixture is left standing for 10-15 min.

Evaporate the solution in a porcelain bowl in a water bath up to one-fourth of its initial volume. See that the ammonium iodide crystals formed when the liquid evaporates are not overheated on the bowl walls. If the solution becomes yellow during evaporation, add $NH_3 \cdot H_2O$ or H_2O_2 to it dropwise. Cool the bowl containing the solution with ice and rapidly filter off the crystals on a glass filter No. 2. Dry the ammonium iodide in a desiccator over phosphoric anhydride up to a constant mass (3-5 days). Write the equation of the reaction.

Purify the dry ammonium iodide by sublimation in the apparatus shown in Fig. 62*b*. Take off the "head" of the apparatus and carefully spill the ammonium iodide onto its bottom. See that the substance does not get onto the walls of the vessel.

Assemble an apparatus for the preparation of dry ammonia (Fig. 62*a*). To do this, put solid sodium hydroxide (*wear eye protection and handle the alkali with a porcelain spoon!*) into two-neck bottle *1* or a Wurtz flask. Pour a 25% ammonia solution into dropping funnel *2*. Put soda lime or a granulated alkali into drying columns *3*. Pour glycerin or vaseline oil (a bubble counter) into wash bottle *4*.

Displace all the air from the apparatus with a stream of ammonia. Connect the apparatus to cock *2* of the sublimation apparatus (Fig. 62*b*). Fill the system with ammonia by opening cocks *2* and *1*, and heat the part of the apparatus accommodating the ammonium iodide in a tubular furnace until sublimation begins (about 200 °C) (*use a thermocouple*). Regulate the rate of ammonia flow and of furnace heating so that the ammonium iodide will decompose as little as

possible and will not escape through cock *1*. If during sublimation iodine is deposited on the walls of the apparatus, remove it by heating them with a burner while passing a strong stream of ammonia through.

When sublimation has been completed, transfer the substance from the vessel into a weighed weighing bottle and weigh it. Calculate the yield in per cent. Store ammonium iodide in a sealed ampoule.

6. Preparation of Potassium Iodide. Put 1-2 g of iron shavings or reduced iron, 25 ml of water, and the calculated amount of iodine into a small conical flask. Slightly heat the mixture up to complete

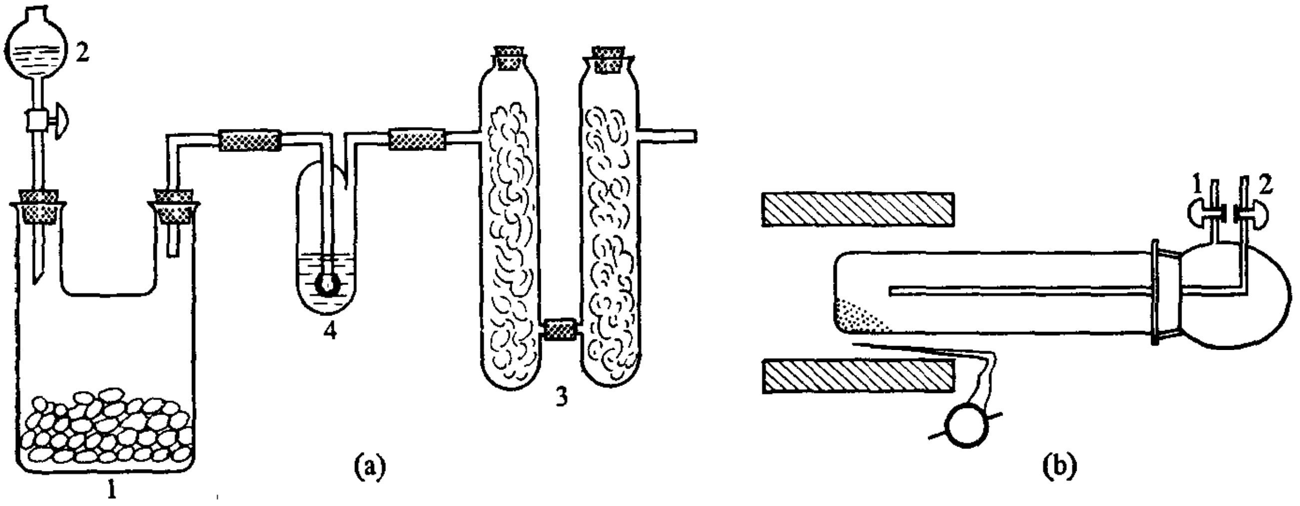


Fig. 62. Apparatus for preparing ammonia (*a*) and apparatus for purifying ammonium iodide by sublimation in an ammonia stream (*b*)

dissolution of the iodine. Pour the liquid over the unreacted iron into another small flask, heat it up to boiling, and gradually add a solution containing 7 g of potassium carbonate in 20 ml of water to the boiling solution. What do you observe? What is the precipitate?

Continue heating the reaction mixture until a transparent sample of the solution no longer contains iron. (How can this be checked?) Keep the volume of the solution constant.

When the reaction has terminated, filter off the precipitate and evaporate the solution in a bowl on a water bath until a film forms. What is the composition of the precipitated crystals? Cool the solution to 0 °C, filter off the crystals on a Büchner funnel, and dry them in a drying cabinet. Transfer the dry crystals into a previously weighed weighing bottle, weigh it, and calculate the yield in per cent. Write the equations of all the reactions.

7. Preparation of Cadmium Iodide. Put 5 g of cadmium precipitated by zinc from a cadmium salt solution and 6 g of freshly sublimed iodine into a 250-ml flask provided with a reflux condenser (see Fig. 21). Pour in 50 ml of distilled water and boil the mixture up to complete decolouration of the solution. Filter the latter through a

paper filter, evaporate the filtrate on a water bath until crystals appear, and then cool them to 0 °C. Examine the shape of the crystals under a microscope. Filter off the crystals on a Büchner funnel, wash them on a filter with small portions of cold water, transfer them to a watch glass, and dry them in a desiccator over phosphorus(V) oxide up to a constant mass. Transfer the substance to a previously weighed weighing bottle. Calculate the yield in per cent.

8. Preparation of Potassium Bifluoride. (*Perform the experiment in a fume cupboard, wear rubber gloves!*). Pour 25 ml of a 40% hydrogen fluoride solution into a platinum (nickel) bowl. Cool the bowl with an ice and salt mixture. Introduce the calculated amount of potassium carbonate in small portions into the acid solution while stirring (until evolution of a gas stops), after which check the reaction of the solution. The latter should be slightly acidic (a pH of about 6). Dilute the solution with distilled water (40 ml) and filter it through a smooth filter placed in a paraffin-coated glass funnel. Evaporate the filtrate in a platinum bowl on a water bath until crystallization begins, next cool it to 0 °C, and filter off the precipitated crystals on a Büchner funnel. Transfer the crystals onto a watch glass and dry them in a desiccator over phosphorus(V) oxide up to a constant mass (at least a day). Write the equation of the reaction. Calculate the yield in per cent.

Fig. 63. Test tube for dehydrating potassium bifluoride in vacuum

For dehydration, place the platinum (nickel) crucible with the prepared salt (~5 g) into a test tube with a standard ground-glass joint (Fig. 63). Preliminarily weigh the crucible and the salt with an accuracy up to 0.01 g. Connect the test tube to a vacuum system. Evacuate it (10^{-1} mmHg) first at room temperature during 10-20 min, and then at 150 °C on an oil bath or a bath with Wood's alloy. Dehydrate the substance up to a constant mass. Calculate the composition of the product according to the change in its mass.

9. Preparation of Potassium Bromate. Pour 30 ml of a 40% potassium hydroxide solution into a porcelain beaker and carefully heat it. Add 1 ml of bromine to the solution from a dropping funnel whose tube must reach the bottom of the beaker. Do this very slowly while continuously stirring the solution. Next saturate the solution with chlorine (for what purpose?).

To determine the end of the reaction, take a small amount of the

solution, dilute it with water, boil it up to complete removal of bromine and chlorine (starch iodide paper should not change its colour), and add phenolphthalein. The colour of the solution should not change. Cool the solution to room temperature, filter off the separated crystals using a Büchner funnel, and dry them in the air. Calculate the yield in per cent.

Heat a small amount of the potassium bromate in a test tube and detect the evolving oxygen. Write the equations of the reactions.

10. Preparation of Iodic Acid. (*Perform the experiment in a fume cupboard!*) Weigh 1 g of iodine in a porcelain bowl, carefully add the

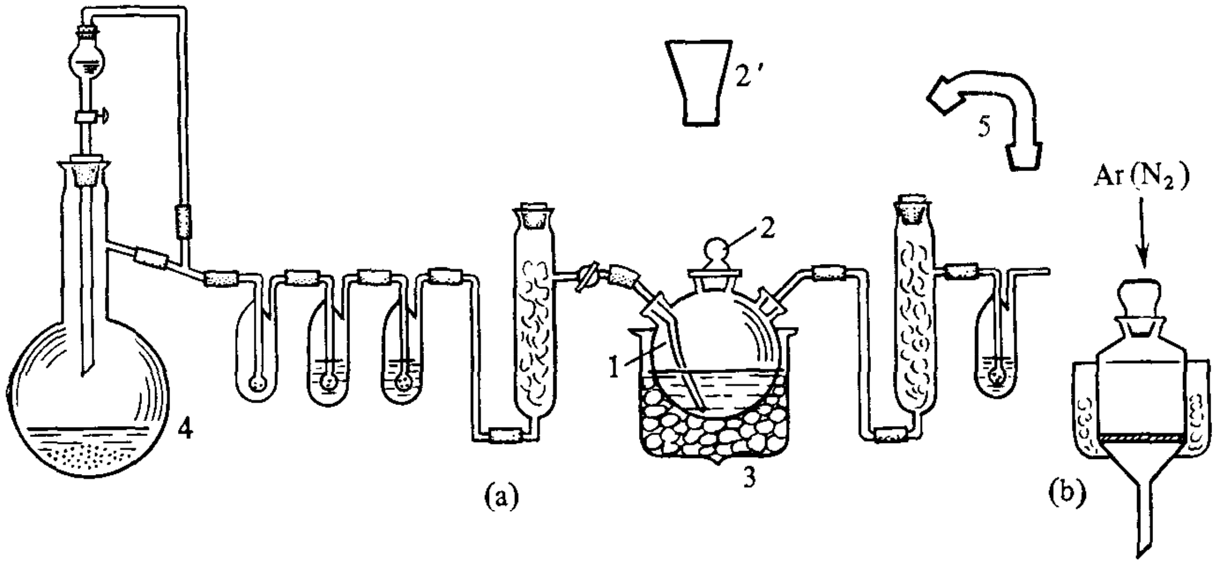


Fig. 64. Apparatus for preparing iodine trichloride (*a*) and funnel with a filtering bottom for filtration in an inert atmosphere with cooling (*b*)

calculated amount of fuming nitric acid ($d = 1.5$), place the bowl on a water bath, and slightly heat it. What is the boiling point of nitric acid of the indicated concentration? What is the highest temperature to which the bath can be heated?

Heat the bowl with its contents until the iodine dissolves completely. Heat the bath up to boiling and evaporate the solution until dry only after the colour of iodine vanishes. Acquaint yourself with the properties of iodic acid (see p. 101).

11. Preparation of Iodine Trichloride. Assemble an apparatus as shown in Fig. 64*a*. Prepare chlorine in flask *4* by reacting concentrated hydrochloric acid with potassium permanganate. Dry and pure chlorine condenses in flask *1* placed in vessel *3* containing dry ice. There should be about 20 ml of liquid chlorine. Rapidly substitute funnel *2'* for stopper *2* and introduce 10 g of crushed dry iodine in small portions into the flask during 20-30 min. After introducing each portion, close the flask with the stopper and shake the reaction mixture. After introducing all the iodine, disconnect flask *1* from the apparatus for preparing chlorine and let it stand in

the dry ice for one hour. Remove the excess chlorine from the flask by evaporation at room temperature and then under a vacuum by a water-jet pump.

Transfer the iodine trichloride from the flask into a weighed drawn out test tube. Cool the tube with dry ice and rapidly seal it (*wear eye protection!*). Weigh the test tube with the substance and the remaining fragments of the tube. Calculate the yield in per cent. Write the equation of the reaction. Use the prepared iodine trichloride in the following syntheses.

12. **Preparation of Tetrachloroiodic Acid Tetrahydrate.** Prepare iodine trichloride or use the already prepared substance. Put 10 g of the iodine trichloride into a round-bottomed flask provided with a dropping funnel on a ground-glass joint. Pour 30 ml of concentrated hydrochloric acid preliminarily saturated with hydrogen chloride at 0 °C from the funnel into the reaction flask. The density of the acid must be at least 1.19 g/cm^3. Saturate commercial hydrochloric acid with hydrogen chloride at 0 °C during 1-1.5 h. Stir the contents of the flask by vigorously shaking it during 5-10 min and cool it to —30 °C. After 30 min, replace the dropping funnel with transfer tube *5* (see Fig. 64*a*) and transfer the reaction mixture onto a glass filter No. 2 adapted for filtration without the access of air with cooling (Fig. 64*b*) and filter it. Put the formed crystals in a glass weighing bottle.

13. **Preparation of Potassium Tetrachloroiodate Dihydrate.** Dissolve 18 g of iodine trichloride in 20 ml of concentrated hydrochloric acid with vigorous stirring in a round-bottomed flask with a ground-glass stopper. Cool the solution to 0 °C and add to it a mixture of 5 g of potassium chloride and 12 ml of a concentrated hydrochloric acid solution. Dilute the reaction mixture to twice its volume with concentrated hydrochloric acid cooled to 0 °C.

After 30-40 min, rapidly filter off the formed potassium tetrachloroiodate crystals on a filter No. 2 and wash them two or three times with concentrated hydrochloric acid cooled to 0 °C. Dry the crystals in a desiccator over sulphuric acid. Weigh the substance and seal it in an ampoule. Calculate the yield in per cent.

12 SULPHUR, SELENIUM, TELLURIUM

Indicate the position of the sulphur subgroup elements in Mendeleev's periodic table of the elements, the electron configurations and the size of their atoms, and the oxidation states they exhibit.

12.1 SULPHUR AND ITS COMPOUNDS

Write the electron configuration of a diatomic sulphur molecule and compare it with that of an oxygen molecule.

PROPERTIES OF SULPHUR

Rhombic Sulphur. Pour 4-5 ml of chloroform into a dry test tube (*in a fume cupboard!*) and spill in a sulphur powder in small portions, shaking the contents of the tube, until a saturated solution forms. Filter the solution into a porcelain bowl (do not wet the filter with water, why?), cover it with a glass, and let it stand in the fume cupboard for slow evaporation. Put a drop of the solution on a slide, cover it with a cover glass, and observe under a microscope how the crystals grow. Draw the sulphur crystals.

Monoclinic Sulphur. Fill a small porcelain or chamotte crucible with sulphur, and slowly melt it. The melt should occupy at least half of the crucible. Cool the latter until a crystalline crust forms. When the crust almost covers the melt, rapidly pour out the remaining molten sulphur into a beaker of water. Examine the crystals formed with a magnifying glass and draw them.

Dissolve two or three of the crystals in chloroform on a watch glass, and after evaporation of the solvent, examine the shape of the newly formed crystals. What structure of the molecules corresponds to the obtained sulphur modifications?

Changes in Sulphur When Heated. Half fill a test tube with pieces of sulphur and, while holding it in your hand with the aid of forceps, slowly heat it in the flame of a burner. Watch the melting and the subsequent changes in the colour and viscosity of the sulphur. Explain the phenomena that occurred.

Preparation of Plastic Sulphur. Heat sulphur until it boils and pour it out in a thin stream into a crystallizer with cold water. Extract the solid substance from the water and dry it between sheets of filter paper. Test the ductility of the sulphur and its solubility in chloroform. Keep part of the sulphur for the next lesson and again study its physical properties. What molecules does plastic sulphur consist of?

HYDROGEN SULPHIDE

Hydrogen sulphide is poisonous! Perform all experiments with it in a fume cupboard. Immediately take a student poisoned by hydrogen sulphide from the laboratory into the fresh air or let him or her inhale pure oxygen.

Preparation. Put 1-2 g of iron sulphide into a test tube and pour in 5-8 ml of a 20% hydrochloric acid solution. Close the tube with a stopper provided with a drawn out gas-discharge tube (see Fig. 42).

Properties. 1. What odour does the evolving gas have? Light the hydrogen sulphide with a burning splinter, hold a wet piece of litmus paper over the flame, and watch how its colour changes. Write the equation of the reaction.

2. Introduce the cold lid of a crucible into the hydrogen sulphide flame. What appears on the surface of the lid? Write the equation of the reaction.

3. Pour bromine water, chlorine water, and acidified solutions of potassium permanganate and dichromate into separate test tubes. Pass a stream of hydrogen sulphide through all the tubes. What happens? Write the equation of the reactions. What property of hydrogen sulphide is indicated by the occurring phenomena?

Test an aqueous hydrogen sulphide solution with litmus. What do you observe? Find the dissociation constants of hydrosulphuric acid in a textbook.

METAL SULPHIDES

Preparation of Metal Sulphides from the Elements. (*Perform the experiment in a fume cupboard!*) *Copper Sulphide.* Fill one-third of a test tube with sulphur and heat it up to boiling. The sulphur vapour should fill the entire tube. Hold a piece of copper gauze or foil with pincers, heat it in the flame of a burner until red hot, and rapidly introduce it into the sulphur vapour. What happens? Write the equation of the reaction. How does copper sulphide react with water and hydrochloric acid?

Aluminium Sulphide. Weigh 1 g of aluminium powder and the calculated amount of finely triturated sulphur, and thoroughly mix the reactants. Spill out the mixture in a mound onto a metal plate and put a magnesium ribbon in the middle so that its upper end protrudes 1-2 cm above the mixture. Ignite the magnesium (*in a fume cupboard with a lowered glass window!*). How can you explain the hydrogen sulphide odour of the aluminium sulphide?

Throw a small amount of aluminium sulphide into a test tube with hot water. Explain what occurs. Write the equations of the reactions.

Iron Sulphide. Prepare 5 g of a mixture of sulphur and a powder of reduced iron taken in equivalent amounts, transfer it into a test tube, secure the latter in the clamp of a stand, and heat the bottom of the tube on a strong flame until a reaction begins. As soon as this occurs, remove the burner. What is observed? Write the equation of the reaction. How can you prove that the compound obtained is a sulphide? Test the reaction of iron sulphide with hydrochloric acid.

Zinc Sulphide. Using equivalent amounts of zinc (a powder) and sulphur, prepare about 5 g of a mixture, put it on a metal plate, and heat it (*carefully, in a fume cupboard!*). What occurs? Write the equation of the reaction. See how zinc sulphide interacts with water and hydrochloric acid.

Preparation of Metal Sulphides by an Exchange Decomposition Reaction. *Precipitation with Ammonium Sulphide.* Pour 2 ml each of solutions of iron(II), manganese(II), zinc, cadmium, lead, antimony, and copper salts into separate test tubes. Add 2 ml of an ammonium sulphide solution to each tube. Note the colour of the formed precipitates. Write the equations of the reactions and the values of the solubility products of the sulphides of these metals (see Appendix 1, Table 12). Using the concept of the solubility product, explain the process of precipitation of sulphides under these conditions.

Test the reaction of a 3% hydrochloric acid solution with the metal sulphides, taking a small amount of them. Explain the different reaction of hydrochloric acid with metal sulphides.

Precipitation with Hydrogen Sulphide. Test the effect of hydrogen sulphide on the solutions of the same salts using hydrogen sulphide water for this purpose or passing hydrogen sulphide from a Kipp gas generator through the solutions (thoroughly wash the gas-discharge tube after each experiment).

Explain why precipitates form only in some of the solutions. What substances form when hydrogen sulphide reacts with solutions of iron(II) salts? Classify the studied metal sulphides according to their solubility in water and acids.

Properties of Water-Soluble Sulphides. Dissolve sodium sulphide in water. Pour the solution into two test tubes. Test the reaction of the sodium sulphide solution with indicators (phenolphthalein, litmus). How can you explain what occurs? Pass a stream of carbon dioxide through the solution in the second tube. Note the odour of the evolving gas. Write the equation of the reaction.

What will happen to the sodium sulphide if it is left in an open beaker? Explain the processes occurring in a sodium hydroxide solution when hydrogen sulphide is passed through it.

SULPHUROUS ACID ANHYDRIDE

(*Perform the experiments in a fume cupboard!*)

Preparation. 1. What forms when sulphur burns in the air?

2. Put several sodium sulphite crystals into a test tube and add 2-3 drops of a 70% sulphuric acid solution. Write the equation of the reaction and explain the direction of the process on the basis of the law of mass action.

3. Assemble an apparatus (see Fig. 53*a*), replacing the second wash bottle with a dry U-tube (*wear eye protection!*). Pour a small amount of a 96% sulphuric acid solution into the first wash bottle. Put the U-tube into a bath cooled by a mixture whose temperature should be below —10 °C. Put 5-10 g of copper shavings into a Wurtz flask and pour the calculated amount of a 96% sulphuric acid solution over them. Heat the reaction flask strongly in a sand bath until the intensive evolution of gas begins, after which remove the burner. Watch the temperature of the cooling mixture. What gathers in the U-tube? Write the equation of the reaction.

Properties. 1. Pour several drops of liquid sulphurous acid anhydride into a 50-ml thick-walled bottle (see Fig. 53*b*). After its evaporation, cover the mouth of the bottle with a stopper provided with a drawn out glass tube. Invert the bottle with the gas, and in this position immerse it into a bath with water. Explain what occurs. Write the equation of the reaction. What equilibria set in when sulphurous acid anhydride is dissolved in water?

What salts form consecutively when sulphur dioxide is passed into a sodium hydroxide solution? What products form when these salts are roasted?

2. Pour 5 ml each of chlorine water, bromine water, and of potassium permanganate and dichromate solutions acidified with sulphuric acid into separate test tubes. Pass a stream of sulphur dioxide gas into the test tubes in turn or pour in a small amount of a sulphurous acid solution. What happens? Write the equations of the reactions. What properties does sulphur dioxide exhibit?

3. Pour 1-2 ml of hydrogen sulphide water and a sulphurous acid solution into a test tube. What occurs? Write the equation of the reaction. What properties does sulphurous acid exhibit in the given case? Identify the products formed when gaseous sulphur dioxide and hydrogen sulphide react.

4. Pour 2 ml of a fuchsin (magenta) solution into a test tube and pass a stream of sulphur dioxide through it. What happens? Boil the solution. Comment on your observations. How can the occurring phenomena be explained?

SULPHURIC ACID AND ITS SALTS

Properties of Sulphuric Acid. (*Perform the experiments in a fume cupboard!*) *Interaction of Concentrated Sulphuric Acid with Water.* Pour 10-15 ml of water into a beaker, measure its temperature, and without extracting the thermometer, add 2 ml of a 96% solution of sulphuric acid. Record the thermometer readings. In what sequence must water and concentrated sulphuric acid be poured together to prepare solutions of various concentrations?

Action of Sulphuric Acid on Organic Substances. **1.** Immerse a splinter into a test tube containing a small amount of concentrated sulphuric acid. What occurs?

2. Prepare 2-3 ml of a sulphuric acid solution (1 : 1). Wet the tip of a glass rod with this solution and make an inscription on a sheet of white paper. Carefully heat the paper to dry it. What happens? What properties of sulphuric acid do the above experiments indicate?

3. Put 10 g of powdered sugar into a 50-ml beaker, wet it with water until a thick paste forms, and then add 3-5 ml of concentrated sulphuric acid. Rapidly stir the contents with a glass rod and see what happens. What gaseous substances are obtained?

Action of Sulphuric Acid on Non-Metals. Pour 2-3 ml of a 96% sulphuric acid solution into each of two test tubes, introduce a small piece of sulphur into one of them and coal into the other, and carefully heat them. What occurs? Write the equation of the reaction.

Action of Sulphuric Acid on Metals. Pour 2-3 ml of concentrated sulphuric acid into a test tube and lower several pieces of iron wire into it. What is observed? Carefully heat the test tube. Do you notice any change now? What properties does sulphuric acid exhibit in this case? What is the difference between the action of concentrated and dilute sulphuric acid on metals? What explains the greater strength and stability of sulphuric acid in comparison with sulphurous acid?

Thermal Stability of Sulphates. 1. Put 1-2 g of sodium bisulphate into a small porcelain bowl or crucible. First carefully heat it, and then strongly roast it. What compounds form? Write the equations of the reactions.

2. Put several iron(II) sulphate crystals on the lid of a porcelain crucible, heat them, and then strongly roast them. Hold litmus paper wetted with water over the crystals. What happens? Write the equation of the reaction.

3. Run a similar experiment with gypsum and Glauber salt.

What does the different thermal stability of the oxygen-containing salts of sulphur and of the corresponding acids depend on?

SODIUM THIOSULPHATE

Preparation. Put 3.5 g of sodium sulphite and 50 ml of water into a small conical flask. Weigh 2.5 g of flowers of sulphur and, after wetting the sulphur with ethanol (why?), transfer it into the flask with the sodium sulphite solution. Heat the mixture up to boiling. The end of the process is featured by a neutral reaction of the solution with litmus. Filter the hot solution and evaporate it on a water bath up to the beginning of crystallization. Filter off the crystals that precipitated after cooling in a Büchner funnel. Write

the equation of the reaction. Write the graphic formula of sodium thiosulphate.

Properties. 1. Dissolve several sodium thiosulphate crystals in a small amount of water and add 1-2 ml of a hydrochloric acid solution. What is observed? Write the equation of the reaction.

2. Put several sodium thiosulphate crystals on the lid of a crucible and first carefully, and then strongly heat them. What do you observe? Write the equation of the reaction. What substances form when sodium thiosulphate decomposes? Prove this.

3. Pour 3-4 ml of chlorine water into a test tube and add a sodium thiosulphate solution dropwise until the chlorine odour vanishes. Write the equation of the reaction. Why is sodium thiosulphate called "antichlorine"?

4. Perform a similar experiment with iodine water. Write the equation of the reaction.

Why are various products of sulphur oxidation obtained when chlorine and iodine water react with sodium thiosulphate? What forms when bromine water reacts with sodium thiosulphate? What is the commercial name of sodium thiosulphate?

12.2 SELENIUM AND TELLURIUM

Selenium and tellurium compounds are poisonous! The experiments are demonstrated by the instructor!

Selenium and its compounds are strong poisons. Selenium halides, hydrogen selenide, and the oxygen compounds of selenium soluble in water are the most toxic.

Symptoms of poisoning are irritation of the respiratory tracts and eyes, a protracted cold in the head, and headaches.

As regards the nature of their action on a human organism, tellurium and its compounds are similar to the inorganic compounds of selenium and arsenic. Hydrogen telluride is the most toxic. Tellurium(IV) oxide and aqueous solutions of the salts of tellurous and telluric acids are also toxic. Only tellurium ("metallic") is not toxic if it gets into an organism.

Indications of poisoning by tellurium salts are an odour of garlic of the exhaled air, a headache, accelerated breathing and pulse, a feeling of fatigue and dizziness.

SELENIUM(IV) AND TELLURIUM(IV) OXIDES

Properties of Selenium(IV) Oxide. 1. Test the reaction of selenium(IV) oxide with water, and also with solutions of acids and alkalies. Write the equations of the reactions.

2. Add solutions of tin(II) chloride and sulphurous acid to selenous acid solutions in separate test tubes. Heat the contents of the

tubes. What is observed? What properties of selenous acid do these reactions indicate? Write the equations of the reactions.

3. Add potassium permanganate and dichromate solutions respectively to two test tubes containing selenous acid solutions acidified with sulphuric acid. Heat the contents of the test tubes. What do you observe? Write the equations of the reactions. What properties does selenous acid exhibit in this case?

Properties of Tellurium(IV) Oxide. 1. Test the reaction of tellurium(IV) oxide with water, and also with solutions of sodium hydroxide and hydrochloric acid with heating. Write the equations of the reactions.

2. Add tin dichloride and sulphurous acid solutions respectively to two test tubes containing solutions of tellurium(IV) oxide in hydrochloric acid diluted with water. Heat the contents of the test tubes. Comment on your observatioss. Write the equations of the reactions. What property do the salts of tetravalent tellurium exhibit in the given reactions?

Compare the physical and chemical properties of sulphurous, selenous, and tellurous acids (see Appendix 1).

SUPPLEMENTARY EXPERIMENTS AND SYNTHESES

1. Preparation of Hydrogen Sulphide from Its Elements. (*Perform the experiment in the presence of your instructor!*) Assemble an apparatus as shown in Fig. 65 and check its tightness. Put 1-2 g of sulphur into test tube *2* and close it with a stopper provided with two bent tubes (test tube *2* can be replaced with a Wurtz test tube). Pour a small amount of a copper sulphate solution into wash bottle *3*. Connect a Kipp gas generator producing hydrogen to test tube *2* via wash bottle *1* containing concentrated sulphuric acid. Check the tightness of the apparatus again.

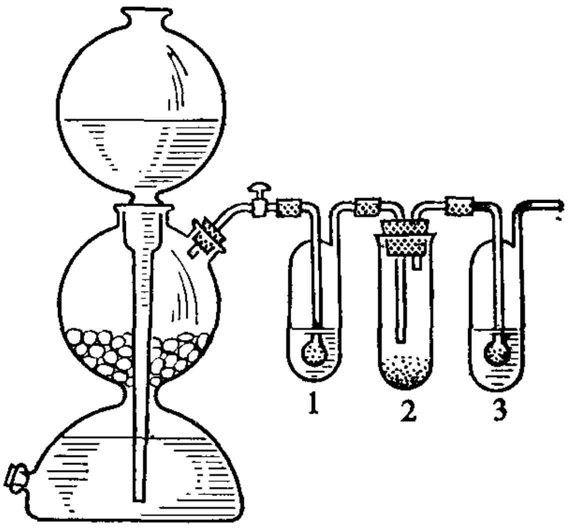


Fig. 65. Apparatus for preparing hydrogen sulphide from its elements

Pass a stream of hydrogen through the apparatus and test its purity (how can this be done?). Without stopping the supply of hydrogen and carefully heating test tube *2* with the flame of a burner, melt the sulphur. What happens to the copper sulphate solution? Remove the burner and let the apparatus cool in a stream of hydrogen. Write the equations of the reactions.

2. Preparation of Sodium Bisulphide. Assemble an apparatus as shown in Fig. 66. Fill drying columns *4* with phosphorus(V) oxide placed on glass wool. Weigh 2-2.5 g of metallic sodium, wash it with benzene and diethyl ether, thoroughly remove the oxide film from its surface, cut the sodium up into small pieces, and put them into test tube *2*. Pour 75 ml of absolute ethanol into 150-200-ml round-bottomed flask *1*. Fill the apparatus with dry argon (nitrogen) via tube *3*.

By turning test tube *2* about the ground-glass joint during 10-15 min, introduce the taken amount of sodium into reaction flask *1*.

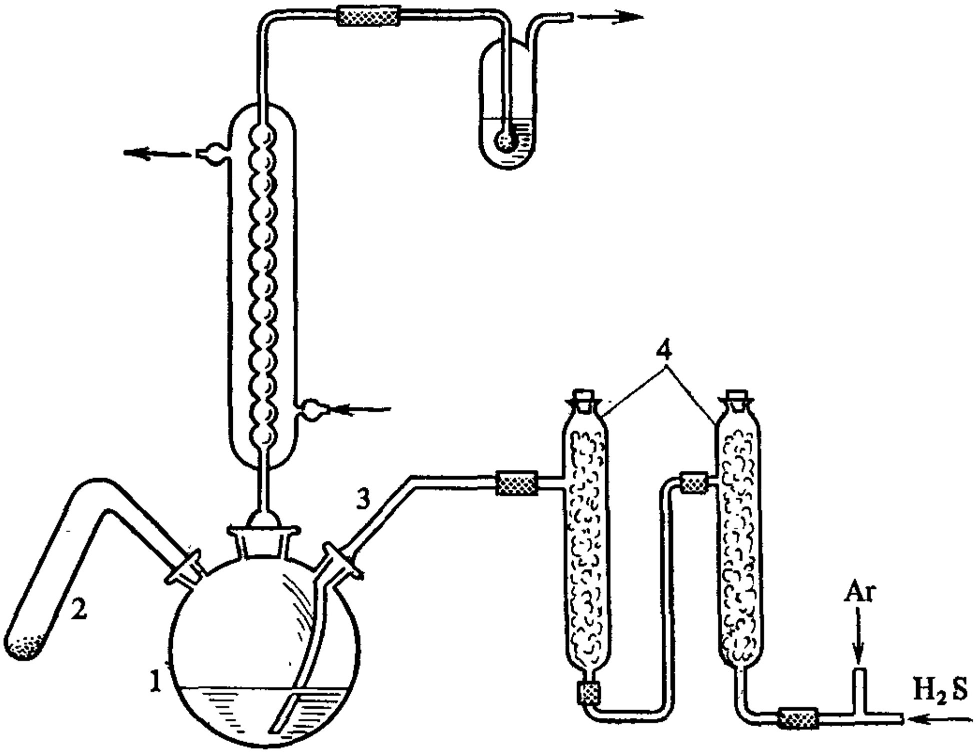


Fig. 66. Apparatus for preparing **sodium bisulphide**

After complete dissolution of the metal (the solution may be slightly turbid), pass a strong stream of dry hydrogen sulphide through tube *3* during one hour.

If a substantial amount of sulphur precipitates during the reaction, filter the solution in an inert argon or nitrogen atmosphere through a glass filter No. 2 (see Fig. 64*b*). The receiver for the filtrate must be clean and dry. Keep the inert atmosphere and add 250-300 ml of absolute diethyl ether to the filtrate, introducing it in 20-25-ml portions every 10 minutes.

Separate the precipitated sodium bisulphide crystals by means of a glass filter No. 2, wash it with absolute diethyl ether, and transfer it for drying into a test tube with a ground-glass joint. Connect the test tube to a vacuum system and keep it under a vacuum (10^{-1} mmHg) at 20°C during 30 minutes. Put the dry preparation

into a previously weighed weighing bottle, weigh it, and calculate the yield in per cent.

3. **Preparation of Sodium Sulphide.** Assemble an apparatus as shown in Fig. 67. Put 0.2 g of finely triturated highly pure sulphur into test tube *1* with a ground-glass joint, and lower the tube into a beaker with a mixture of dry ice and acetone. Connect a source of dry ammonia (see Fig. 62*a*) to cock *3* of the apparatus, open cock *4*, and fill the apparatus with ammonia. Put 2 g of metallic sodium thoroughly purified of oxide films and washed with benzene and diethyl ether onto filter *2*. Pass ammonia through the apparatus until test tube *1* is filled with liquid ammonia up to one-third of its volume, after which disconnect the apparatus for preparing ammonia. Close cocks *3* and *4*, remove the cooling beaker from test tube *1*, and put dry ice wetted with acetone into beaker *5* with double walls. Repeatedly remove the cooling agent and supply it to test tube *1* and beaker *5* so that the liquid ammonia will dissolve the metallic sodium on filter *2*. (Open cock *4* from time to time to relieve the excess pressure of the ammonia.) By strongly cooling test tube *1*, "suck in" the solution of metallic sodium in liquid ammonia into the solution of sulphur in liquid ammonia. Repeat this operation several times. After the reaction has terminated, remove the cooling, and let the ammonia evaporate through cock *4*. Connect the apparatus (cock *3*) through a drying column with soda lime or an alkali to a water-jet pump and evacuate it during 20 min. Transfer the preparation into a previously weighed weighing bottle, weigh it, and calculate the yield in per cent.

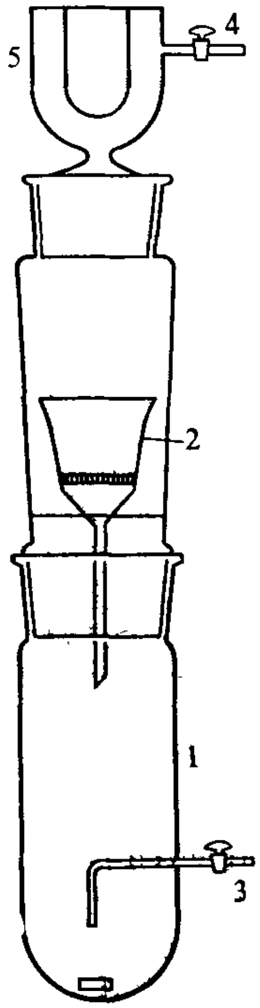


Fig. 67. Apparatus for preparing sodium sulphide

Carefully (*with your instructor's assistance!*) wash the vessel with small portions of ethanol because traces of unreacted metallic sodium may remain on the walls of the test tube and the filter. (When the sodium residues are slaked with ethanol, the sodium may ignite!)

4. **Preparation of Sulphur Chlorides.** *(a) Preparation of a Mixture of Sulphur Chlorides.* (*Perform the experiment in a fume cupboard!*) Melt

3 g of sulphur in a retort and cover its walls with a thin layer of liquid sulphur by turning it. Connect the retort as indicated in Fig. 68 to an apparatus for preparing dry chlorine. Immerse the neck of the retort into a small flask cooled by ice. Close the mouth of the flask with cotton wool. Slightly heat the part of the retort containing

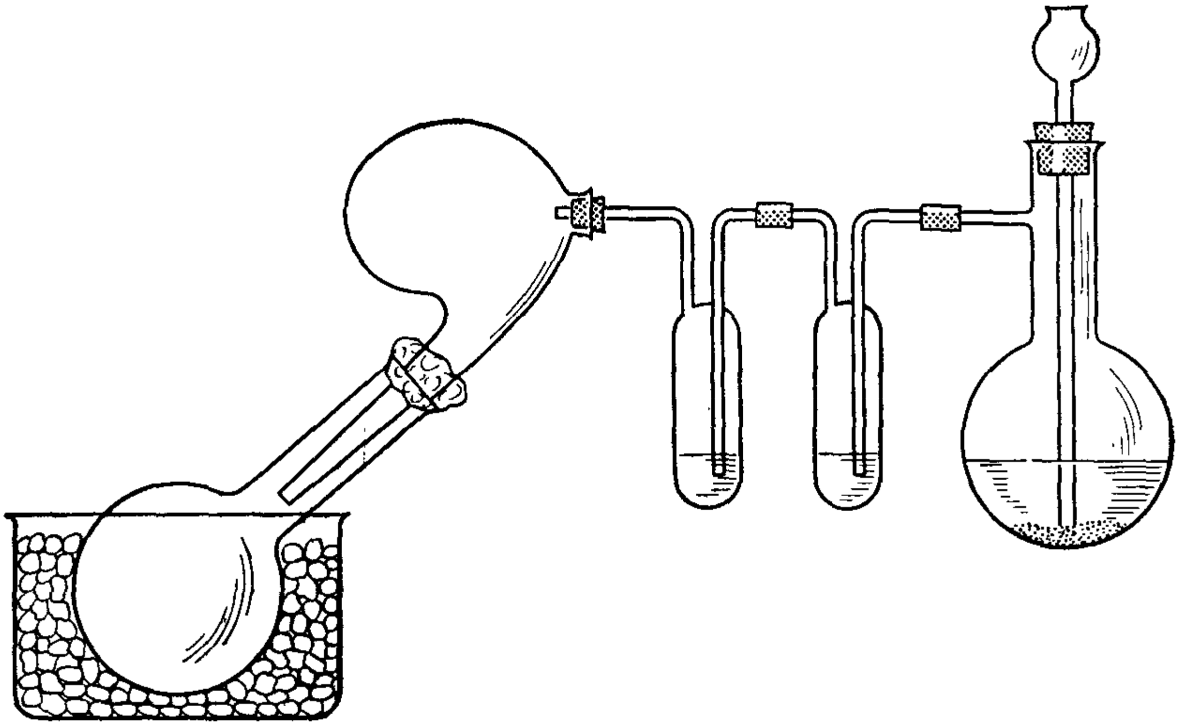


Fig. 68. Apparatus for preparing sulphur chlorides

the sulphur with the flame of a burner and pass a stream of dry chlorine through the retort. What gathers in the receiver? Write the equation of the reaction. Stop the experiment when 5-6 ml of sulphur chloride gather. What colour does the compound have?

Pour the liquid into four test tubes (*in a fume cupboard, wear eye protection!*). Carefully add water to one of them, and introduce some sulphur into another one. What happens? Write the equations of the reactions. Keep two test tubes with sulphur chloride for the following experiments.

(*b*) *Preparation of Sulphur Dichloride.* (*Perform the experiment in a fume cupboard!*). Put a test tube with sulphur chloride obtained in the preceding experiment into a beaker with ice and pass a strong stream of dry chlorine through the liquid. How does the colour of the liquid change?

Pour a little of the obtained liquid into a small porcelain bowl and leave it in the fume cupboard. What happens? Write the equations of the reactions.

5. **Preparation and Purification of Sulphur Monochloride.** (*Perform the experiment in a fume cupboard!*) Assemble the setups shown

in Fig. 69*a* and *b*. Put 13 g of commercial sulphur into a test tube (Fig. 69*a*). Heat the tube in a sand bath or a bath with Wood's alloy up to 150-200°C.

Pass a stream of dry chlorine through the molten sulphur during two hours at a rate such that virtually the entire chlorine is absorbed by the molten sulphur. After this, cool the reaction mixture to room

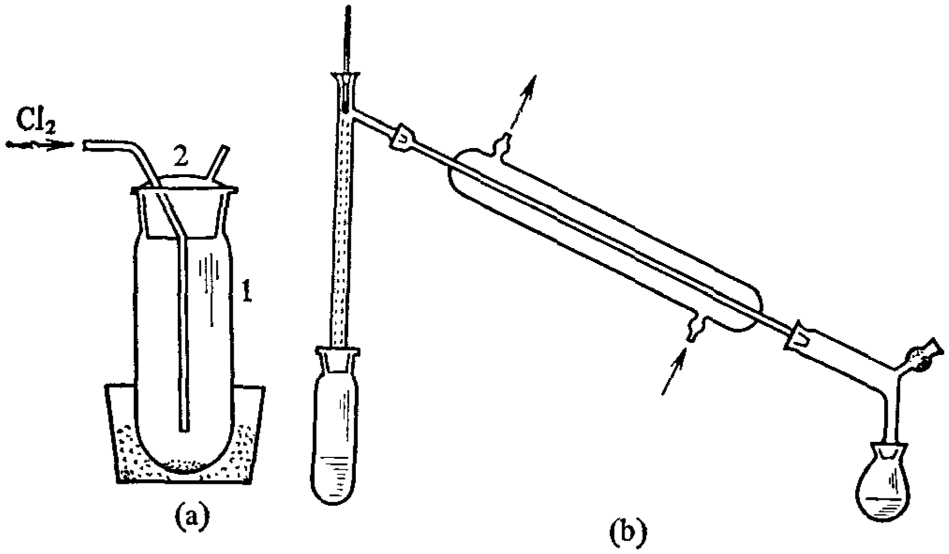


Fig. 69. Setups for the chlorination of sulphur (*a*) and the fractional distillation of sulphur chlorides (*b*)

temperature. If the sulphur solidifies, repeat the treatment with chlorine at 150 °C. Carry out chlorination until the reaction mixture cooled to room temperature remains liquid.

Distil off the product from the test tube. Transfer it into an apparatus for the fractional distillation of liquids at atmospheric pressure (see Fig. 20). Carefully heat the liquid with the flame of a burner until it boils. Collect the fraction boiling at a temperature above 130 °C.

Pour over the liquid into a weighed drawn out test tube. Seal the tube to form an ampoule (*wear eye protection!*).

Weigh the ampoule with the substance and the remnants of the test tube. Calculate the yield in per cent.

6. Preparation of Thionyl Chloride. Assemble an apparatus as shown in Fig. 70*a* and check its tightness. Put 15 g of phosphorus pentachloride onto the bottom of dry retort *1*. (This compound readily hydrolyzes!) Switch on water cooler *2*. Pass a stream of thoroughly dried sulphur dioxide through the retort. What occurs? When the reaction slows down, slightly heat the retort while carefully shaking it. Stop the heating after the entire phosphorus pentachloride reacts. Write the equation of the reaction.

Disconnect the cooler and the retort from flask *3* and connect dephlegmator *4* with thermometer *5* via a ground glass joint to flask *3*. Heat flask *3* on an electric stove, and gather the fraction boiling

at 80-85 °C in small flask *6* cooled by ice. Close the receiver with a stopper. Calculate the yield in per cent.

Pour a small amount of the thionyl chloride into a beaker with water (*in a fume cupboard, lower its glass window!*). What happens?

7. Preparation of Sulphuryl Chloride. Before performing this synthesis, dry activated carbon in a vacuum (10^{-2} mmHg) in a test tube and heat it during 40-50 min with the flame of a burner.

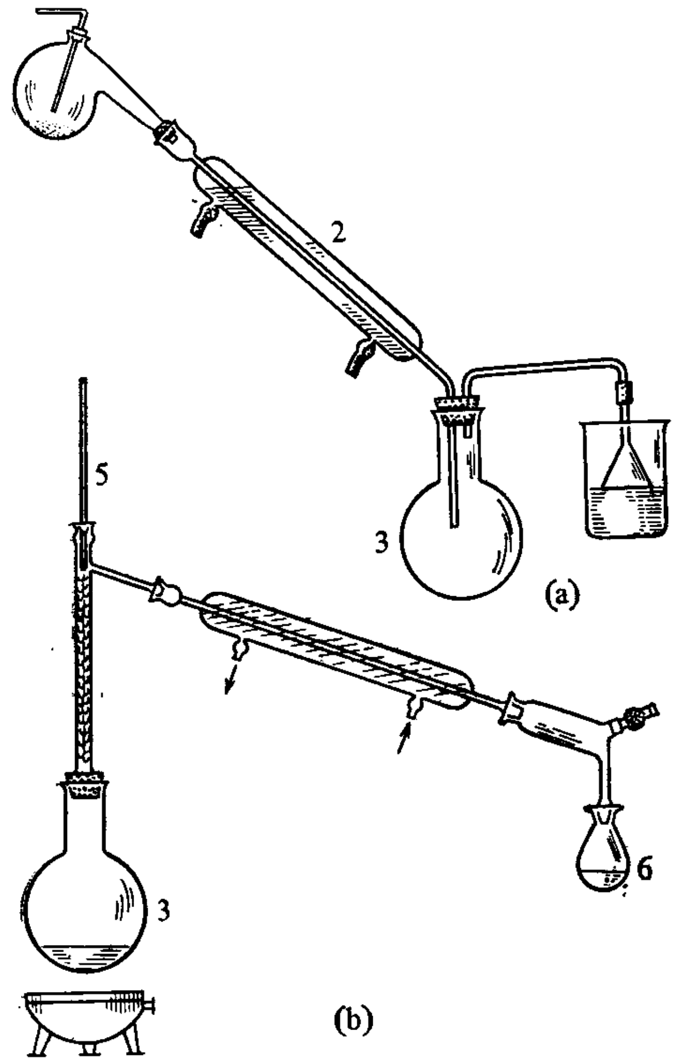


Fig. 70. Apparatuses for preparing thionyl chloride (*a*) and purifying it by distillation (*b*)

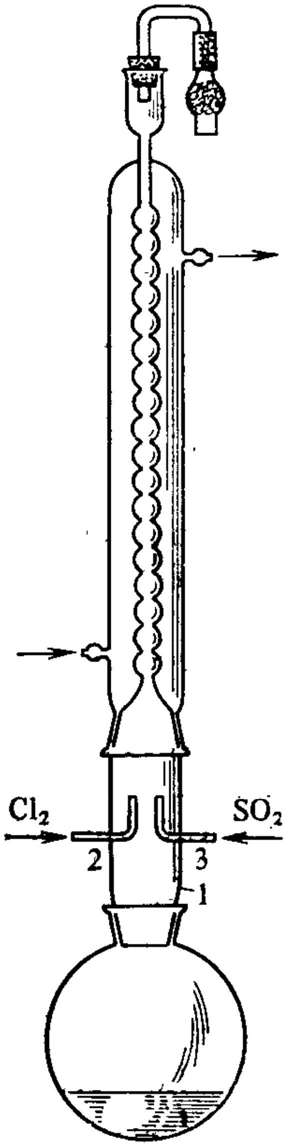


Fig. 71. Apparatus for preparing sulphuryl chloride

Put the dried activated carbon loosely on a glass wool substrate into each of the bulbs of a cooler on standard ground glass joints (the number of bulbs should be at least six). The carbon should occupy at most one-half of the volume of a bulb. Camphor may be used instead of the activated carbon.

Assemble an apparatus as shown in Fig. 71. Connect cooler *4* to a 100-ml round-bottomed flask with the aid of special adapter *1*. Connect apparatuses for preparing dry chlorine (see Fig. 61) and

sulphur dioxide (see Fig. 73) to tubes *2* and *3* and simultaneously pass both gases through the system at the same rate. First leave the cooler jacket without water, and after sulphuryl chloride begins to gather in the flask, cool the bulbs with a weak stream of cold water. Cool the flask in a bath with ice. Stop the reaction after preparing 50-60 ml of sulphuryl chloride.

To purify the sulphuryl chloride, connect the receiver flask to an apparatus for distillation under atmospheric pressure provided with a dephlegmator (see Fig. 70). Heat the flask in a water bath and distil the substance, collecting the fraction that boils at 68-70 °C.

8. **Preparation of Sulphuric Acid by the Contact Process.** Assemble an apparatus as shown in Fig. 72. Fill gas meter *1* with oxygen and

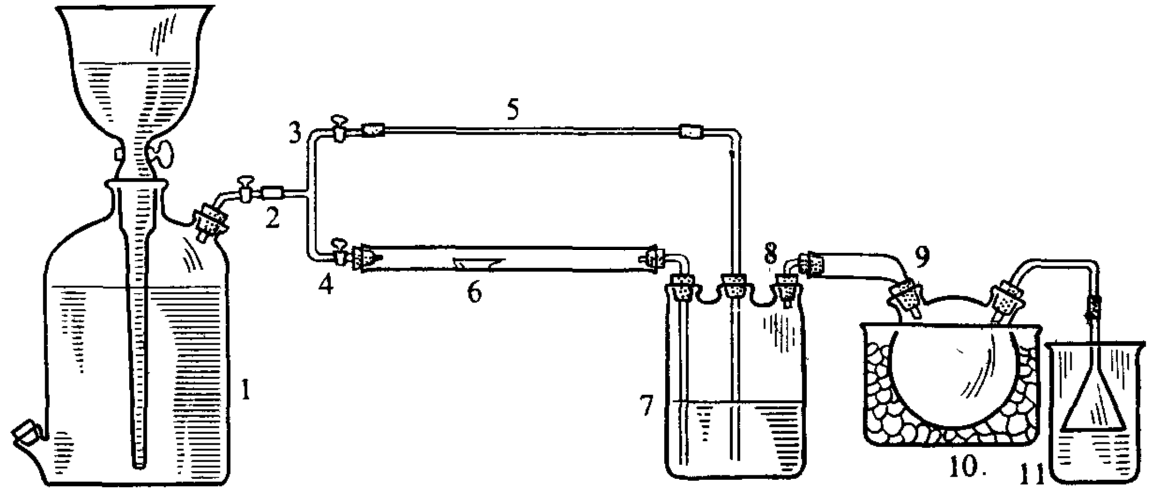


Fig. 72. Apparatus for preparing sulphuric acid by the contact process

connect it via three-way tube *2* with cocks *3* and *4* to tubes *5* and *6* (tube *6* should be made from a refractory material). Pour a small amount of concentrated sulphuric acid into three-neck bottle *7*. Connect gas-discharge tube *8* emerging from the three-neck bottle to bent refractory tube *9*. Put platinized asbestos* into the horizontal part of tube *9*. Place two-neck flask *10*, which is the receiver, into a crystallizer with ice mixed with sodium chloride. Connect a funnel to the gas-discharge tube of the receiver and put it into beaker *11* over an alkali solution.

Check the tightness of the apparatus and fill it with oxygen. Put a small amount of sulphur into a boat, ignite it in the air, and put it into tube *6*. Regulate the oxygen stream from the gas meter so

* Prepare platinized asbestos as follows: put 5 g of purified asbestos into a bowl and pour a 1-2% chloroplatinic acid solution over it. Transfer the fibres impregnated with the solution into a porcelain crucible and roast them first carefully, and then strongly on a blowtorch. Store the prepared catalyst in a jar with a ground-glass stopper. Roast the platinized asbestos without fail before each experiment.

that you will be able to count the bubbles of the gases emerging from the tube in bottle *7*. What must be the ratio of the volumes of oxygen and sulphur dioxide when preparing sulphuric acid anhydride (sulphur trioxide)? Strongly heat the platinized asbestos. Prove that the substance obtained is sulphuric acid anhydride.

9. Preparation of Sulphuric Acid by the Chamber Process. Assemble an apparatus shown in Fig. 73. Spill sodium bisulphite into flask *1* and pour a 70% sulphuric acid solution into funnel *2*. Put copper

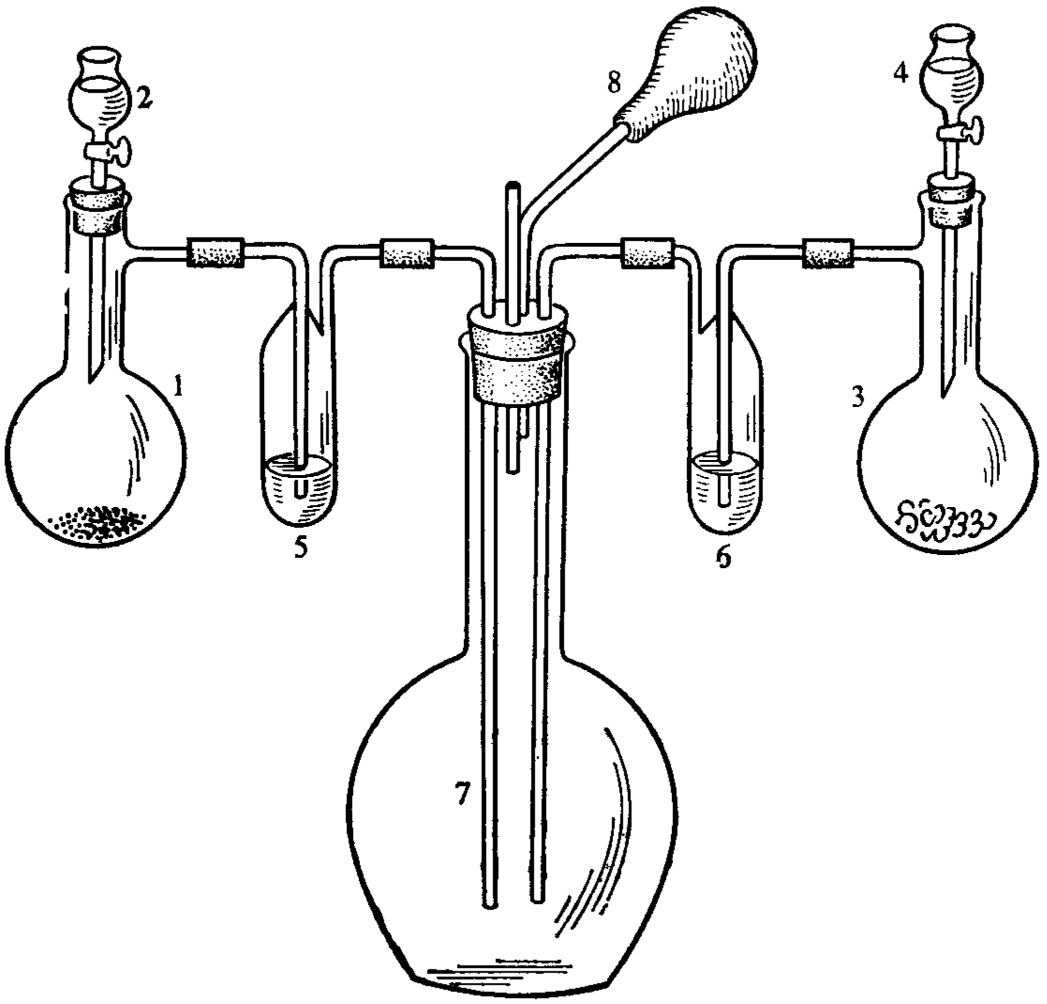


Fig. 73. Apparatus for preparing sulphuric acid by the chamber process

shavings into flask *3*, and pour a concentrated nitric acid solution into funnel *4*. Pour concentrated sulphuric and nitric acid solutions into wash bottles *5* and *6*, respectively.

Open the cock of funnel *4* and add nitric acid dropwise. As soon as flask *7* is filled with nitrogen(IV) oxide vapour (the colour must be very intensive), open the cock of funnel *2* and add sulphuric acid dropwise into flask *1*. Watch the change in the colour. What crystals are deposited on the walls of flask *7*? Using rubber bulb *8*, add 2-3 ml of water into flask *7* and rinse its walls. What happens to the crystals? What gas fills the flask now?

Open the stopper of flask *7* and watch the change in the colour of the gas. Again add 2-3 ml of water, rinse the flask, and pour out the liquid into a beaker. Prove that a solution of sulphuric acid has been prepared. What impurities does the acid contain? Write the equations of all the occurring processes.

What industrial processes exist for the production of sulphuric acid? How can the purest acid be produced?

10. Preparation of Copper Sulphate Pentahydrate (Copper Vitriol). Pour 20-30 ml of water into a 100-ml beaker, and transfer into it the mixture remaining in a Wurtz flask after the reaction of copper with

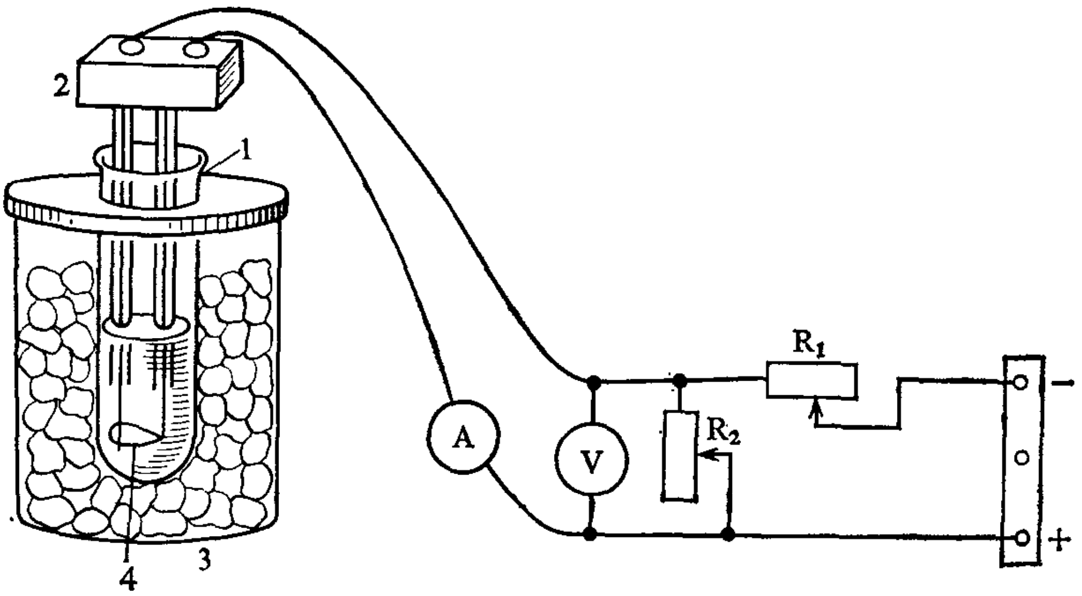


Fig. 74. Apparatus for preparing potassium persulphate

sulphuric acid. Heat the formed mixture to 70-80 °C, filter the solution, introduce 2-3 g of lead(IV) oxide into it (why?), and boil it (what precipitates?). Again filter the solution and collect the filtrate in a porcelain bowl. Evaporate the filtrate on a water bath until a crystalline film appears on the surface of the liquid, and let it stand for crystallization.

Transfer a drop of the hot solution onto a slide, cover it with a cover glass, and examine the crystals under a microscope. Filter off the crystals formed in the bowl on a Büchner funnel, wash them with a small amount of ice water, transfer them onto a glass plate and dry them in the air at room temperature. Put a little of the salt in a crucible and heat it first slightly, and then strongly. What do you observe? Explain the change in colour when copper vitriol is dehydrated. Write the equations of the reactions.

11. Preparation of Potassium Persulphate. Assemble an apparatus shown in Fig. 74. Put 100 ml of a potassium bisulphate solution saturated at 0 °C (see Appendix 1, Table 1) into test tube *1*. Immerse

block *2* with electrodes into the test tube. Fill outer Bunsen beaker *3* with water and ice and connect the electrodes to a 24-V d-c source. Use rheostats R_1 and R_2 to set a current of 4 A. See that the temperature of the electrolyte in the test tube does not exceed 8 °C. Perform electrolysis during one hour.

Write the equation of the reaction. Indicate the substances that evolve at the electrodes. Transfer the evolved crystals onto a glass filter No. 3 (about 400 mesh), suck off the filtrate, and wash the

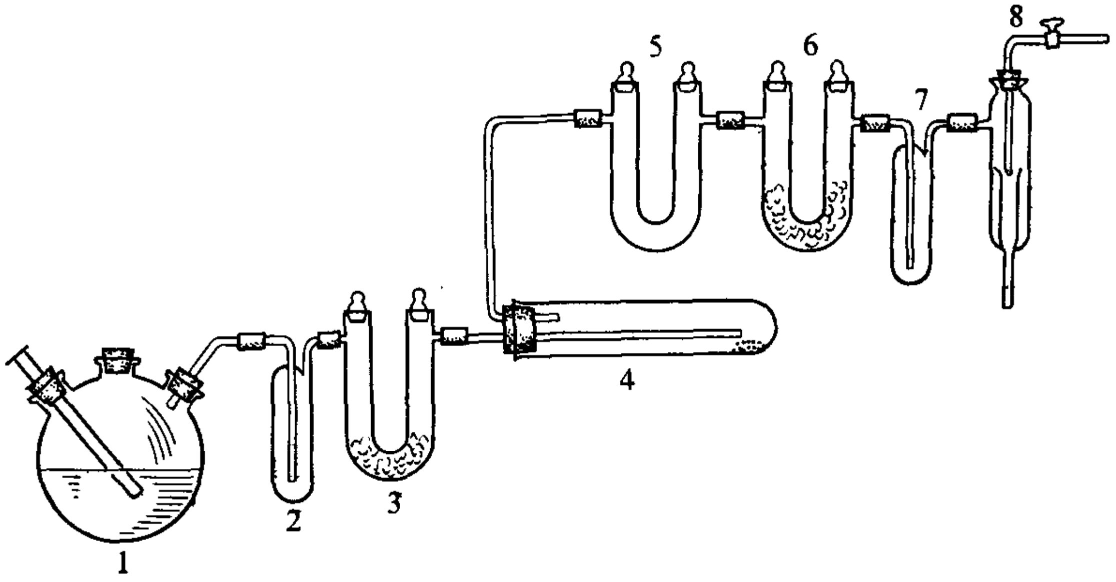


Fig. 75. Apparatus for preparing selenium(IV) oxide

crystals with ethanol. Dry the crystals in a desiccator over sulphuric acid, weigh them, and determine the yield relative to the current in per cent.

Prepare 20 ml of a solution of the obtained compound saturated at room temperature. Pour 3 ml of the solution into each of three test tubes. Add to the first tube 1 ml of a 1 *N* sulphuric acid solution, one drop of silver nitrate, and one drop of a 1 *N* manganese sulphate solution. Heat the tube. Add to the second tube 1 ml of a 1 *N* chromium sulphate solution and 2 ml of a 1 *N* sodium hydroxide solution. Pour into the third tube 1 ml of a 1 *N* sodium hydroxide solution and 1 ml of a 1 *N* manganese sulphate solution. Comment on your observations. Write the equations of the reactions.

What compounds are called peracids? What are the features of their structure?

12. Preparation and Properties of Selenium(IV) Oxide. *Selenium compounds are very poisonous! Hand in the prepared substances and residues of selenium preparations to the laboratory assistant. Run all experiments with selenium in a fume cupboard! After work, thoroughly wash the ware and your hands.*

Assemble an apparatus as shown in Fig. 75. Pour 50-100 ml of a concentrated nitric acid solution into 250-ml three-neck flask *1*,

and connect empty wash bottle *2* to it for trapping any splashed out nitric acid. Fill U-tubes *3* and *6* with a loose layer of phosphorus anhydride mixed with glass wool. Leave U-tube *5* empty for trapping the residues of selenium(IV) oxide. Pour a little water into wash bottle *7* connected to a water-jet pump.

Weigh 0.2-0.5 g of selenium and put it into refractory tube *4* sealed at one end (about 30 cm in length and 4 cm in diameter).

Lower several pieces of copper shavings into three-neck flask *1*, and carefully switch on water-jet pump *8*. When the entire apparatus is filled with nitrogen oxides, heat the part of the tube where the selenium is with the flame of a gas burner. First heat carefully, and then more strongly. What occurs?

As copper dissolves in the nitric acid, add new portions of copper shavings to it. When the entire selenium is oxidized, disconnect the flask with nitric acid, and suck a stream of dry air through the apparatus. Extract the prepared selenium(IV) oxide from the tube, put it into a weighing bottle, and weigh it. Determine the yield in per cent. Write the equations of the reactions. Test the properties of selenium(IV) oxide (see p. 116). Hand in the preparation to your instructor.

13. Preparation and Properties of Tellurium(IV) Oxide. *Tellurium compounds are poisonous! Run experiments with tellurium in a fume cupboard! Even negligible amounts of tellurium and its compounds getting into a human organism cause an odour of garlic that does not vanish for a long time.*

After completing work, thoroughly clean up your workplace and wash the ware with concentrated hydrochloric acid or aqua regia. *Wash your hands with soap. Hand in the prepared substances and residues of tellurium preparations to the laboratory assistant.*

Put 3-5 g of powdered tellurium into a 0.5-litre beaker. Wet the tellurium with distilled water, pour 30-50 ml of concentrated hydrochloric acid into it, and add 10-30 ml of concentrated nitric acid in small portions. Heat the reaction mixture, covering the beaker with a watch glass. If the tellurium does not dissolve completely, dilute the reaction mixture up to one-third of its volume with water, and filter the solution through a fluted filter wetted with a 5% solution of hydrochloric acid. Add 100 ml of hot water (80 °C) to the filtrate while constantly stirring it. What is observed?

Neutralize the solution with ammonia up to a weakly acidic reaction (pH 3-4), using methyl red as an indicator. Test with the indicator as follows: apply several drops of it onto filter paper placed on a glass plate, and in the course of neutralizing the solution being tested take a sample of it with a glass rod and transfer it onto the filter paper with the indicator.

Filter off the precipitated substances (what is its composition?) on a Büchner funnel, rinse it with water to remove chloride ions,

and dry it in a drying cabinet at 105 °C. Determine the yield **in per** cent. Write the equations of the reactions.

Test the properties of tellurium(IV) oxide (see p. 117).

13 NITROGEN

Indicate the position of nitrogen in Mendeleev's periodic table of the elements, the electron configuration and the size of its atom, and the oxidation states it exhibits. Write the electron configuration of a nitrogen molecule. What is the bond multiplicity in it?

13.1 PREPARATION AND PROPERTIES

1. Assemble an arrangement as shown in Fig. 76 and check its tightness. Spill 1-2 g of triturated sodium nitrite into the test tube, pour in dropwise 2-3 ml of a concentrated ammonium chloride solution, and carefully (why?) heat the mixture. Collect the evolving gas and see whether it supports combustion. Write the equation of the reaction of nitrogen preparation.

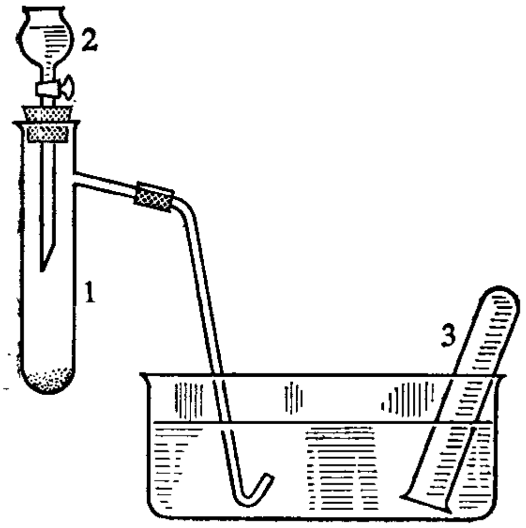


Fig. 76. Arrangement for preparing nitrogen

2. Put a little chlorinated lime into test tube *1*, and pour a concentrated ammonia solution into dropping funnel *2*. Add the ammonia solution dropwise to the chlorinated lime and collect the evolved nitrogen in test tube *3* by putting it over the end of the gas-discharge tube. Write the equation of the reaction. See whether nitrogen supports combustion. How can nitrogen be distinguished from carbon dioxide? What explains the low reactivity of nitrogen? How is nitrogen produced industrially? Where is nitrogen used?

13.2 COMPOUNDS

AMMONIA

Ammonia and nitrogen oxides irritate the respiratory tracts, therefore prepare and work with these substances in a fume cupboard!

Preparation and Properties. 1. Prepare a mixture of 1-2 g of ammonium chloride and 1-2 g of slaked lime (calcium hydroxide). Does

ammonia form? Transfer the mixture into a test tube and close it with a stopper accommodating a bent gas-discharge tube (Fig. 77). Heat the test tube with the mixture. Bring a piece of litmus paper wetted with concentrated hydrochloric acid to the end of the gas-discharge tube (what happens?). Write the equations of the reactions.

Collect the ammonia in a 50-100-ml thick-walled jar (is ammonia heavier or lighter than air?). Close the jar with a stopper containing a capillary and lower it into a bath with water (see Fig. 53*b*). What do you observe after a certain time elapses? What is the solubility of ammonia in water? What equilibrium sets in in the solution? Why is an aqueous ammonia solution a poor electrolyte?

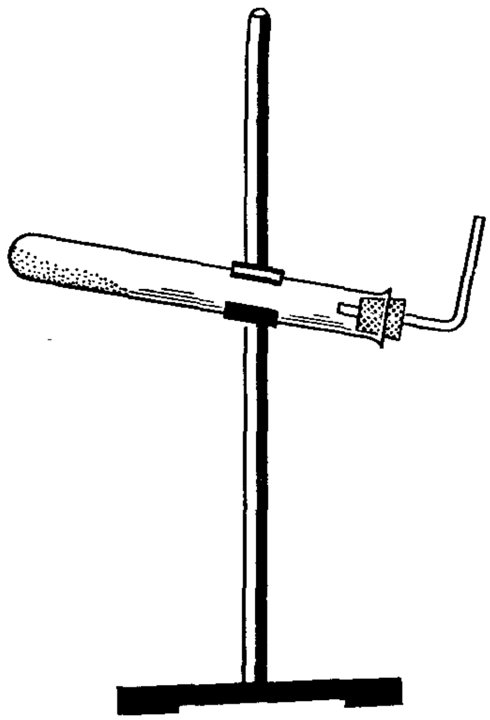


Fig. 77. Setup for preparing ammonia

2. Pour 2 ml of a dilute ammonia solution into a test tube and heat it. How does equilibrium shift in the ammonia-water system when the temperature is changed?

3. Pour 2 ml of a 25% ammonia solution into a test tube and throw a small piece of sodium hydroxide into it. What happens? Explain the observed phenomenon on the basis of the law of mass action. What processes are used to produce ammonia in the industry? Where is ammonia used?

AMMONIUM SALTS

Ammonium Chloride. Put ammonium chloride into a glass tube 20 cm long and 1 cm in diameter. Using two glass rods, press it at the middle of the tube into a layer of 3 cm. At a distance of 2-3 cm from the stopper made in this way spill in a little more ammonium chloride. Put strips of blue and red litmus paper at the mouth of the tube.

Fasten the tube in an inclined position in a clamp of a stand and heat the layer of ammonium chloride below the stopper. What explains the change in the colour of the litmus paper? What law does the rate of gas diffusion observe? Which of the gases obtained as a result of the thermal dissociation of ammonium chloride diffuses more rapidly, and how many times? Write the equation of thermal dissociation of ammonium chloride.

Ammonium Salts of Phosphoric Acid. Put several crystals of one of the ammonium salts of phosphoric acid on the lid of a crucible and heat them. Identify the substance remaining on the crucible lid after heating. Write the equation of the reaction.

Ammonium Sulphate. Put several ammonium sulphate crystals on the lid of a crucible and roast them. Write the equation of the reaction of thermal dissociation of ammonium sulphate.

Ammonium Nitrate. Put several ammonium nitrate crystals on the lid of a crucible and carefully heat them (*in a fume cupboard, lower the glass window!*). Write the equation of the reaction.

How can the different nature of thermal decomposition of ammonium salts be explained? What ammonium salts sublime? How can one prove experimentally that the salts used are ammonium ones?

Using notions of complexing, draw an ammonium ion. What atom is the donor in the given ion and what atom is the acceptor of electrons? What is the coordination number of nitrogen in an ammonium ion? What is the geometric model of an ammonium ion? What type of orbital hybridization occurs when it forms?

HYDRAZINE AND HYDROXYLAMINE

Properties. 1. Pour 5 ml of water into each of two test tubes, and introduce 2-3 drops of hydrazine, hydrazine hydrate, or several crystals of hydrazine sulphate into them. Add several drops of iodine water into one tube. What is observed? Write the equation of the reaction. Add solutions of copper(II) chloride and an alkali into the other tube. Carefully heat its contents. What happens? Write the equation of the reaction. What properties do hydrazine compounds have?

2. Dissolve several crystals of hydroxylamine chloride in 4-5 ml of water. Test the solution with litmus. Add a few drops of iodine water. What occurs? What properties of hydroxylamine are revealed by the given reaction?

What is the structure of hydrazine, hydrazine hydrate, hydrazine sulphate, and hydroxylamine? Do these compounds exhibit oxidizing properties?

OXYGEN COMPOUNDS

(*Perform the experiments in a fume cupboard!*)

Nitrogen(I) Oxide. Assemble an arrangement as shown in Fig. 78. Put 1-2 g of ammonium nitrate in a test tube and carefully heat it. Collect the evolving gas in two small jars over water. Introduce a spoon with burning phosphorus into one jar, and a glowing splinter

into the other one. How can nitrogen(I) oxide be distinguished from oxygen?

Nitrogen(II) Oxide. Assemble an apparatus as shown in Fig. 53*a*, using a U-tube instead of the wash bottles. Pour an amount of a 10% alkali solution into the U-tube such that the level of the liquid in both arms will be higher than the bent part of the tube by 0.5-1 mm.

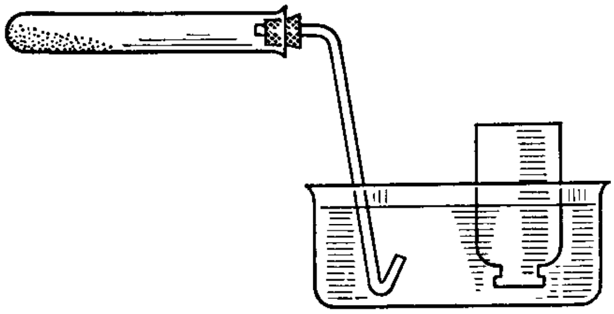


Fig. 78. Arrangement for preparing nitrogen(I) oxide

Put 5 g of copper shavings into the flask and pour in 30 ml of a 33% nitric acid solution through the funnel. If the reaction proceeds slowly, heat the flask somewhat. How can you explain the appearance of the colour of the gases in the flask? Does nitrogen(II) oxide dissolve in water and an alkali? What forms in the U-tube?

1. Gather nitrogen(II) oxide into two small jars (how can this be done?) Test whether a splinter and red phosphorus burn in nitrogen(II) oxide. What happens when nitrogen(II) oxide comes into contact with air? Write the equations of the reactions.

2. Pass a stream of nitrogen(II) oxide through a slightly heated solution of concentrated nitric acid. What is observed? Write the equation of the reaction.

3. Pour 3-5 ml of a freshly prepared saturated iron(II) sulphate solution into a test tube. Pass a stream of nitrogen(II) oxide through the solution. How will the colour of the solution change? Write the equation of the reaction. Heat the solution. Comment on your observations. How is nitrogen(II) oxide produced in the industry?

Nitrogen(IV) Oxide. 1. Put 1-2 g of copper shavings into a Wurtz flask and close it with a stopper provided with a funnel having a long stem. Pour in 5-10 ml of concentrated nitric acid. What gas evolves? Write the equation of the reaction. Collect the nitrogen(IV) oxide in two small jars (how can this be done?) and see whether a glowing splinter and ignited red phosphorus burn in it. Write the equations of the reactions. Which nitrogen oxides give up oxygen more readily?

2. Assemble an apparatus as shown in Fig. 79. Fill U-tube *2* with phosphoric anhydride applied onto glass wool. Put a mixture consisting of 5-7 g of dry lead nitrate and a small amount of clean sand into test tube *1*. Immerse U-tube *3* into a cooling mixture (ice and

salt) and also put a test tube containing 3-5 ml of water into the mixture. Heat test tube *1* with the lead nitrate. What gas is collected in test tube *4* over water when it is placed over the end of the gas-discharge tube from U-tube *3*? What is the composition of the liquid gathering in U-tube *3*?

Disconnect U-tube *3* and rapidly pour out the liquid obtained in it into a test tube with cooled water. What do you observe? Identify the substance gathering on the bottom of the test tube? How can you explain that nitrogen(IV) oxide polymerizes easily?

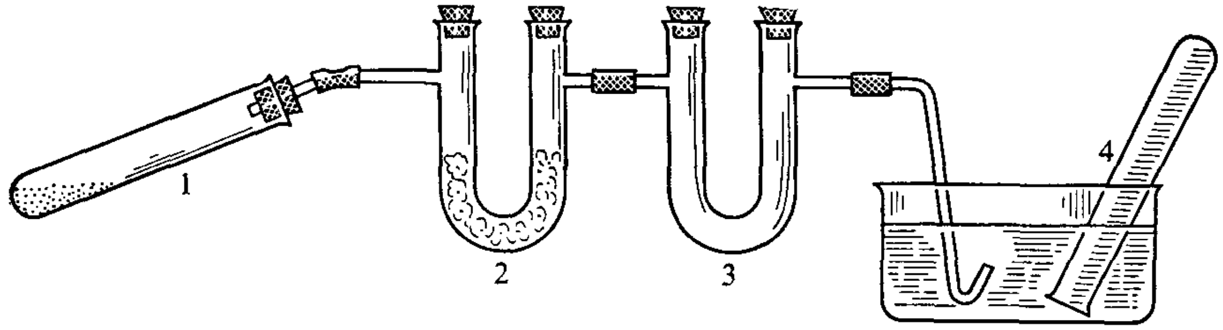


Fig. 79. Apparatus for preparing nitrogen(IV) oxide

Nitrous Anhydride. Assemble an apparatus as shown in Fig. 79, replacing test tube *1* with a small Wurtz flask provided with a dropping funnel, and immerse U-tube *3* into a cooling mixture (ice and salt). Put 1-2 g of starch on the bottom of the flask, and pour 5-6 ml of a 50% nitric acid solution into the dropping funnel.

Adding the nitric acid dropwise to the starch, observe the liquefaction of the nitrous anhydride in U-tube *3*. If no reaction occurs, carefully heat the flask with the reaction mixture. What is the colour of the liquid in U-tube *3*?

Pour out the liquid from the receiver into a beaker with cold water (0 °C). What gas evolves? Write the equation of the reaction. Connect a U-tube with an alkali solution to the gas-discharge tube of the apparatus and pass a stream of the gases through it. What is observed? Write the equation of the reaction.

NITROUS ACID

Preparation and Properties. 1. Dissolve a small amount of potassium nitrite in 1-2 ml of water, cool the solution with ice, and add two or three drops of concentrated sulphuric acid to it. What is observed? Write the equations of the reactions. How can you explain the different strength of nitric and nitrous acids?

2. Pour a potassium nitrite solution into a test tube, acidify it with dilute sulphuric acid, and add several drops of potassium permanganate. What happens? Write the equation of the reaction. Run

a similar experiment with potassium dichromate. What properties of nitrous acid are indicated by this reaction?

3. Add several drops of starch and of a potassium nitrite solution to an acidified solution of potassium iodide. What do you observe? Write the equation of the reaction. Run a similar experiment with potassium bromide, replacing the starch with an organic solvent. What role is played by the nitrous acid in these reactions?

NITRIC ACID

Nitric acid is a strong oxidizing agent. Organic substances may ignite when reacted with the concentrated acid (fuming and anhydrous). *Nitric acid vapour irritates the respiratory tracts. If nitric acid gets on one's skin, it causes serious burns. After thorough washing of the injured part of the skin with water, it should be washed with a 2% soda bicarbonate solution and then synthomycin emulsion applied.*

Perform experiments with concentrated nitric acid in a fume cupboard; wear gloves and eye protection.

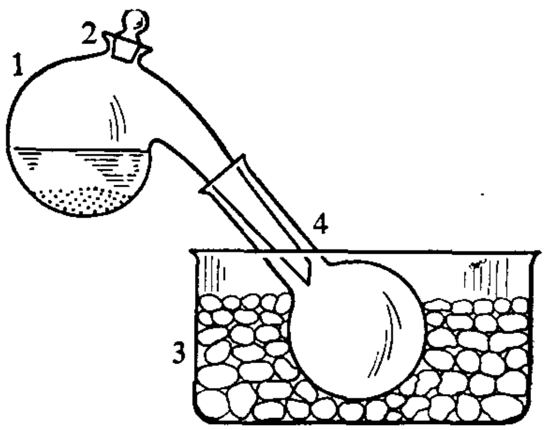


Fig. 80. Setup for preparing nitric acid

Preparation of Nitric Acid from Saltpetre. (*Perform the experiment in a fume cupboard!*) Assemble a setup as shown in Fig. 80. Put 10 g of sodium nitrate into retort *1* and pour in 10 ml of a 96% sulphuric acid solution. Close tubulature *2* with an asbestos stopper. Fill vessel *3* for cooling receiver *4* with water and ice. Carefully heat the retort. What occurs? How can you explain the appearance of brown vapour in the retort? When 4-6 ml of nitric acid are collected in receiver *4*, stop heating the retort. Keep the prepared nitric acid for the following experiment.

Explain from the standpoint of the law of mass action why dry sodium nitrate (saltpetre) and a concentrated sulphuric acid solution are taken to prepare a concentrated nitric acid solution. Why does the reaction mixture have to be heated, but carefully? What are the boiling points of sulphuric and nitric acids? How do nitric acid solutions of various concentrations behave when heated? What is the composition of an azeotropic mixture of nitric acid with water?

Properties. (*Perform the experiments in a fume cupboard!*) **1.** Pour 1-2 ml of freshly prepared concentrated nitric acid into a porcelain bowl. Add one or two drops of concentrated sulphuric acid and carefully add two or three drops of pure turpentine to it with the aid

of a tube or pipette in a fume cupboard (*lower the window!*). What is observed?

2. Pour 2 ml of concentrated nitric acid into each of five test tubes. Secure the first test tube vertically in a clamp of a stand and, while heating the acid, lower a glowing piece of charcoal into it. What happens? Drop a piece of sulphur into the second tube secured in a clamp of the stand and heat the tube. When the tube cools, pour out its contents into water and detect the presence of sulphuric acid. Write the equations of the reactions. Heat the third tube with nitric acid and introduce a piece of wool into it. Comment on your observations.

Pass a stream of hydrogen sulphide through the nitric acid in the fourth test tube. Write the equation of the reaction. Introduce a small amount of copper sulphide into the fifth tube with nitric acid. Explain why it dissolves in nitric acid. Write the equation of the reaction.

3. Test the action of concentrated nitric acid on zinc and tin. Perform the reaction in small porcelain bowls with slight heating (*in a fume cupboard!*). Write the equations of the reactions.

Take two test tubes, put two or three pieces of zinc into one of them and the same amount of tin into the other. Pour 5 ml of a 2% nitric acid solution into each of the tubes and keep them for your next lesson. How can you determine that ammonium salts formed under these conditions? Write the equations of the reactions. What properties of nitric acid do the experiments performed indicate?

4. Prepare 9-12 ml of aqua regia. In what volume ratio do hydrochloric and nitric acids have to be mixed to prepare it? Put small amounts of cinnabar (mercury sulphide) into two porcelain bowls, pour the freshly prepared aqua regia solution over one portion (*carefully!*), and concentrated nitric acid over the other. Put both bowls on a sand bath and heat them. What happens? Write the equations of the reactions.

Why is aqua regia a stronger oxidizing agent than nitric acid? Explain, using the concept of the solubility product, why mercury sulphide does not dissolve in nitric acid, but does in aqua regia.

Salts of Nitric Acid. What products form when potassium, copper, lead, and silver nitrates are roasted? How can the different nature of their decomposition be explained?

SUPPLEMENTARY EXPERIMENTS AND SYNTHESES

1. Liquefaction of Ammonia and Studying of Its Properties. (a) *Liquefaction.* (*Perform the experiment in a fume cupboard in the presence of your instructor!*) Assemble an apparatus as shown in

Fig. 81. Fill two-neck bottle *1* up to one-fourth of its volume with a granulated alkali (*When working with an alkali, wear eye protection! Handle the alkali only with pincers!*) Pour a concentrated ammonia solution into dropping funnel *2*. Pour vaseline or paraffin oil (a bubble counter) into wash bottle *3*. Put a granulated alkali into drying column *4*. What substances should be used for drying ammonia? Fasten a dry bottle over gas-discharge tube *6*. When you have assembled the apparatus, put solid carbon dioxide ("dry ice") into

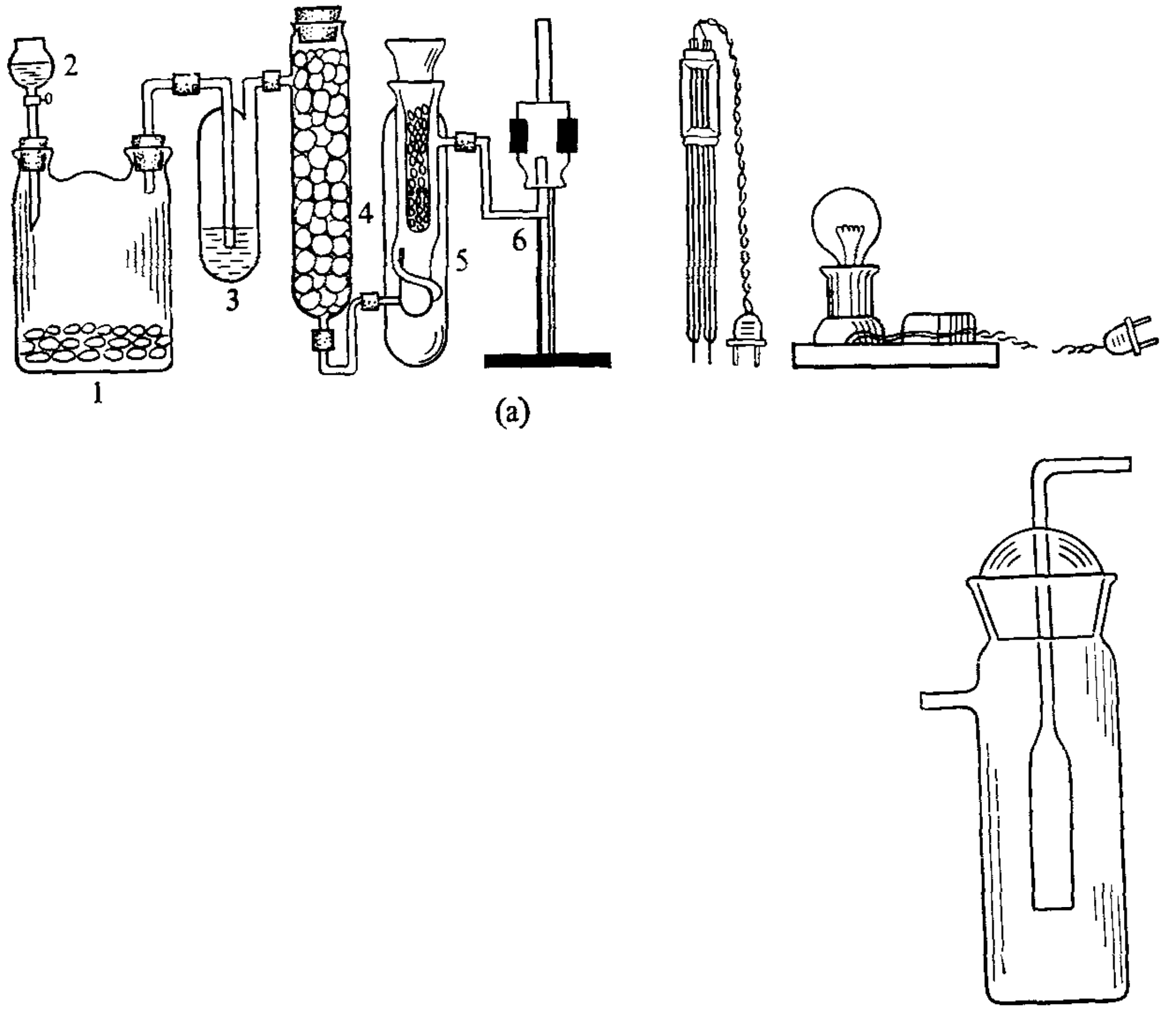


Fig. 81. Apparatus for preparing liquid ammonia (b)

the funnel of vessel *5* for liquefying gases, and carefully add acetone to the carbon dioxide in small portions or place vessel *b* into a beaker with a cooling mixture of the same composition. (*Acetone is flammable! When working with it keep well away from any flame!*)

At what temperature does ammonia liquefy? Open the cock of funnel *2* and add dropwise the concentrated ammonia solution, seeing that the ammonia does not evolve too intensively (the bubble counter!). What do you observe in receiver *5*?

(b) *Dissolving of Ammonia in Water.* After 1-2 ml of liquid ammonia are collected in the receiver, rapidly close it with a stopper provided with a capillary and immerse it into a bath with water

(see Fig. 53*b*). What do you observe after a certain time? What is the solubility of ammonia in water? What equilibria set in when ammonia dissolves in water? Why is an aqueous ammonia solution a poor electrolyte?

(c) *Properties of Liquid Ammonia.* (*Perform the experiment in a fume cupboard in the presence of your instructor!*) When 5-6 ml of liquid ammonia are collected in receiver *5*, disconnect it from drying column *4* and extract the stopper from it. Introduce platinum electrodes into the liquid ammonia (see Fig. 81) and connect them via an incandescent lamp to the mains. What is observed?

Extract the electrodes and drop a small piece of pure metallic sodium thoroughly dried with filter paper into the liquid ammonia. What happens? What explains the colouring of the liquid? Again introduce the electrodes into the liquid ammonia. How did the electrical conductance of the solution change?

Let the ammonia evaporate. What substance remained in the apparatus? *Do not wash the apparatus with water, but hand it in to the laboratory assistant!* Why? What explains the use of ammonia in refrigerating machines?

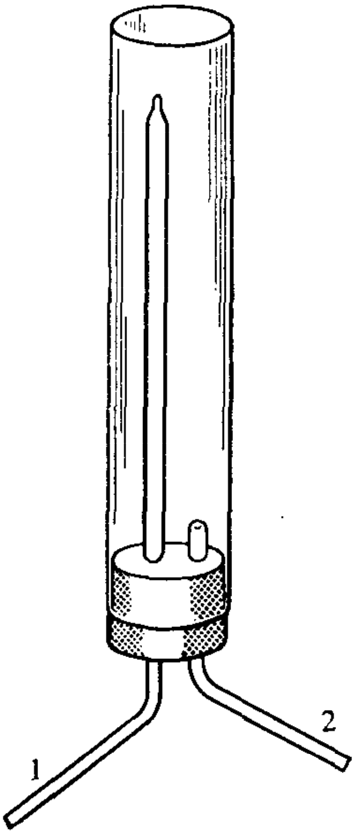


Fig. 82. Device for observing how ammonia burns

(d) *Burning of Ammonia.* Take a wide glass tube 6-8 cm long and close it with a stopper provided with two gas-discharge tubes (Fig. 82). Connect tube *1* to an apparatus for preparing ammonia, and tube *2* to a gas meter with oxygen. Admit a stream of ammonia into tube *1* and bring an ignited splinter up to its mouth. What happens?

Open the gas meter cock and, without stopping the ammonia stream, again bring an ignited splinter to the mouth of tube *1*. What do you observe now? Write the equation of the reaction.

2. Preparation of Magnesium Nitride by Reacting Magnesium with Nitrogen. Assemble an apparatus as shown in Fig. 83 and check its tightness. Fill the apparatus with nitrogen (from a gas meter or cylinder).

Weigh 1 g of magnesium (powder or freshly cut shavings) in porcelain boat *8* and insert it into quartz tube *9* placed in electric furnace *10*. Cut out two or three strips of thin copper gauze and pre-

pare tightly rolled up "sausages" from them. Fasten a test tube in a clamp of a stand and pour 3-4 ml of ethanol into it. (*Wear eye protection!*) Strongly heat a "sausage" in the flame of a gas burner and rapidly introduce it into the test tube with ethanol. What happens? Write the equation of the reaction.

Put the reduced copper into the middle part of porcelain tube *5* in furnace *6*. What role should the copper gauze play? A titanium powder can be used instead of the copper gauze. Titanium heated up to 500-600 °C in a nitrogen atmosphere forms a nitride that absorbs oxygen very well, transforming into titanium dioxide at 400-500 °C.

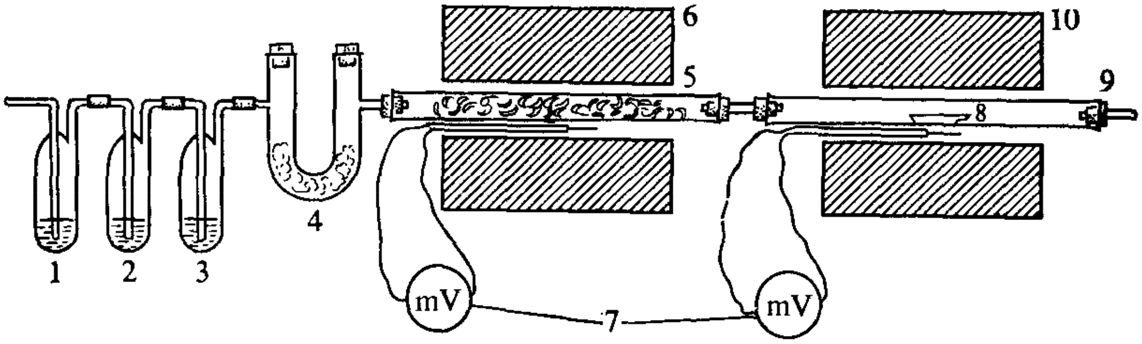


Fig. 83. Apparatus for preparing magnesium nitride by reacting magnesium with nitrogen

Pour an alkaline solution of pyrogallic acid into wash bottle *1*, concentrated sulphuric acid into bottle *3*, and leave bottle *2* empty (what are these wash bottles needed for?). Put a loose layer of glass wool with phosphorus anhydride spilled over it into U-tube *4* (*handle the glass wool with pincers and the phosphorus anhydride with a porcelain spoon*). Again check the tightness of the apparatus and fill it with nitrogen (from a gas meter or cylinder). Without stopping the stream of nitrogen, switch on furnace *6*, and in half an hour, furnace *10*. The temperature of both furnaces must be 400-500 °C (thermocouple *7*). Heat the magnesium in the nitrogen stream for at least two or three hours. When this time elapses, switch off furnace *10* and cool it in a nitrogen stream. Switch off furnace *6* and extract boat *8* from tube *9*. Examine the substance obtained and test the action of water on it. Write the equations of the reactions. Hand in the preparation to your instructor.

3. Preparation of Magnesium Nitride by Reacting Magnesium with Ammonia. Assemble an apparatus as shown in Fig. 84. Put solid sodium hydroxide into two-neck bottle or Wurtz flask *1* (*wear eye protection, handle the alkali with pincers!*). Pour a 25% ammonia solution into dropping funnel *2*. Put a granulated alkali or soda lime into drying column *4*. Pour glycerin or vaseline oil (a gas bubble counter) into wash bottle *3*. Put a reduced copper gauze into porcelain tube *5*. Place 1 g of magnesium powder (prepared before the

experiment) into boat *7* and put it into refractory tube *8*. Pass a stream of ammonia through the apparatus until all the air is displaced from it. The ammonia stream must be sufficiently strong during the entire experiment. Switch on furnace *6* and in half an hour heat refractory tube *8* with the flame of a burner first carefully, and then strongly. Heat during one or two hours. When the magnesium begins to glow, stop the heating. What gas gathers in test tube *9*?

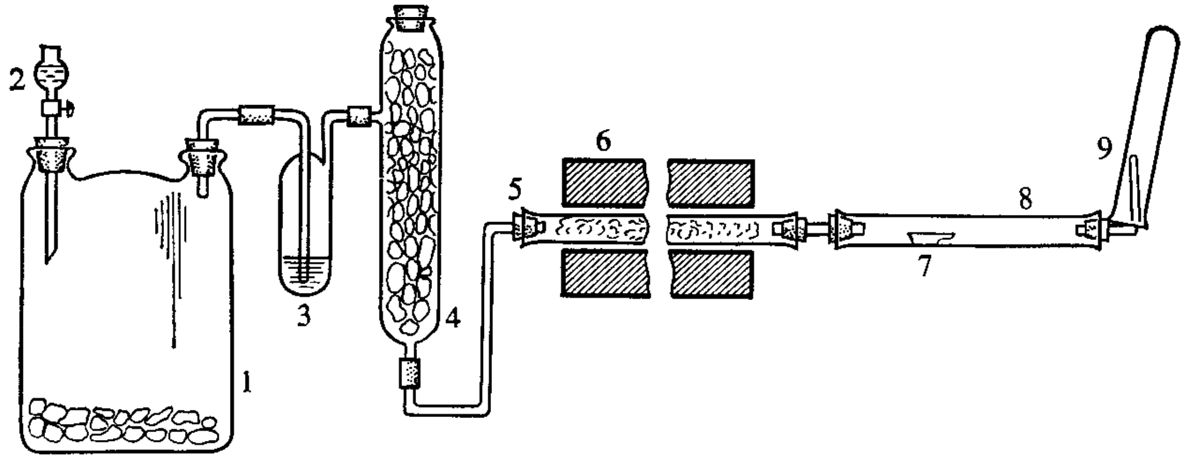


Fig. 84. Apparatus for preparing magnesium nitride by reacting magnesium with ammonia

When the reaction terminates (how can you determine this?), cool the apparatus in a stream of ammonia. Disconnect the two-neck bottle and use a water-jet pump to remove the ammonia from the apparatus. Extract the boat and put it into a weighing bottle for boats or into a test tube closed with a stopper. Weigh it. Determine the yield of magnesium nitride.

Transfer a part of the substance from the boat into a beaker, and pour in two or three drops of a concentrated alkali solution. What gas evolves? Put a small amount of the product on a watch glass and leave it in the air. The odour of what gas can be detected? What happens to the magnesium nitride in the air?

4. **Preparation of Lithium Nitride by Reacting Lithium with Nitrogen.** Assemble an apparatus as shown in Fig. 83. Insert an iron tube into quartz tube *9*. Using pincers, extract a small piece of metallic lithium from the kerosene in which it is stored (*wear eye protection!*), put it in a mortar, and carefully remove the solid crust covering the surface of the metal from all its sides with a thin knife. Lower the cleaned piece of lithium for two or three seconds into a beaker with methanol (why?) and put it into an iron boat. Put the latter into the iron tube.

Displace the air from the apparatus with a stream of nitrogen thoroughly purified from oxygen, and heat tube *9* strongly with the flame of a gas burner until the molten metal (m.p. = 186 °C) begins

to react with the nitrogen. How can you verify this? Only after this remove the flame. Again heat the tube for 10-15 min and then, without switching off furnace *6*, cool it in a stream of nitrogen. Switch off furnace *6*.

Transfer a small amount of the prepared substance from the boat into a beaker and pour a small amount of water over it. Test the evolving gas with moist litmus paper or a strip of filter paper wetted with a mercury(I) nitrate solution. Write the equations of the reactions.

5. **Preparation of Hydrazine Sulphate.** (*Perform the experiment in a fume cupboard!*). Preliminarily prepare a sodium hypochlorite solution. To do this, spill 100 g of ice (prepared from distilled water in the freezing chamber of a refrigerator) into a 300-ml flask and add a sodium hydroxide solution (dissolve 50 g of sodium hydroxide in 100 ml of water). Put the flask in a bath with ice. Pass chlorine during two hours into the cooled solution. When doing this, see that the temperature does not rise above 5 °C.

Pour 30 ml of a 35% sodium hydroxide solution into a 250-ml beaker provided with a mechanical mixer, a thermometer, and a dropping funnel reaching almost to the bottom of the beaker. Cool the beaker with a mixture of ice and sodium chloride, switch on the mixer, and introduce a catalyst—a solution of 0.3 g of manganese(II) sulphate pentahydrate or 0.1 g of manganese(II) chloride tetrahydrate in 1 ml of water. Cool the solution to 0 °C and introduce 7 g of urea into it. Lower the temperature to 5-7 °C below zero and gradually add 63 ml of the filtered sodium hypochlorite solution cooled to the same temperature from the dropping funnel. The temperature even at the end of the reaction must not rise above 10 °C.

After the sodium hypochlorite solution has been added, stir the reaction mixture during 10 min, and then slowly (two degrees a minute) heat the solution on a water bath up to 63-65 °C (use a thermometer!), after which cool the reaction mixture to room temperature.

Pour 70 ml of a 50% sulphuric acid solution into a porcelain beaker. Add the obtained solution to it from the dropping funnel while vigorously mixing (*wear eye protection!*). The temperature must not rise above 40-50 °C. Cool the solution to 22-25 °C (*not lower!*). Filter off the hydrazine sulphate precipitate. Wash it three times with 10-ml portions of water. Dry it in a drying cabinet at 50-70 °C. Weigh the substance. Write the equations of the reactions. Calculate the yield in per cent. How can you convince yourself that the preparation obtained is hydrazine sulphate?

6. **Preparation of Hydrazine Hydrate.** Assemble an apparatus as shown in Fig. 85*a*. Grind 30 g of solid potassium hydroxide into a powder in a porcelain mortar (*wear eye protection!*). Add 30 g of hydrazine sulphate to the powder and thoroughly mix the reactants.

Put the mixture into a copper retort. Close the latter with an asbestos stopper and connect it to a cooler.

Slowly heat the reaction mixture in a sand bath to 120-125 °C. (*Do not permit overheating! The temperature of the bath must not exceed 130 °C.*) At what temperature does hydrazine hydrate boil? Discard the fraction boiling up to 110 °C. Collect the hydrazine hydrate in a preliminarily weighed receiver connected to a cooler via ground-glass joints. Weigh the receiver with the preparation. Calculate the yield. Write the equation of the reaction.

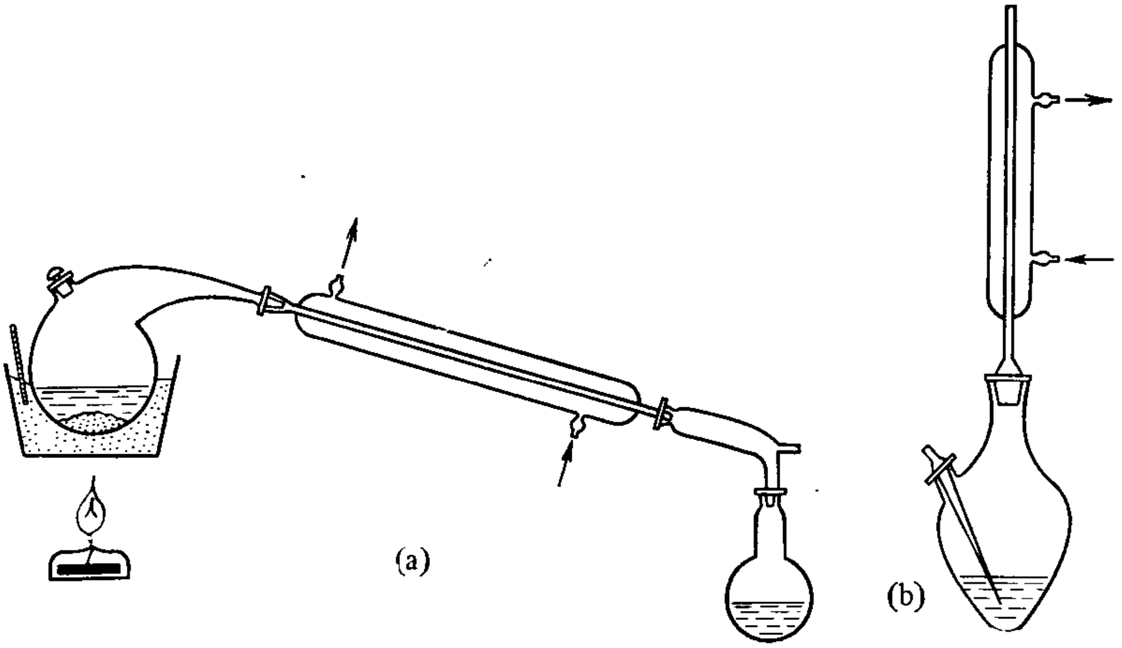


Fig. 85. Apparatus for preparing hydrazine hydrate (*a*) and dehydrating it (*b*)

7. **Preparation of Hydrazine.** Assemble an apparatus as shown in Fig. 85*b*. Put an amount of potassium hydroxide into a two-neck flask provided with a reflux condenser such that there is a 2-3-mm layer of hydrazine hydrate over it. Cool the flask in a bath with ice and transfer the previously prepared hydrazine hydrate into it (*wear eye protection!*). Pass a stream of dry nitrogen through the reaction mixture. Carefully heat the flask until the alkali dissolves completely, then cool the flask to room temperature, and, without stopping the nitrogen stream, replace the reflux condenser with a dephlegmator. Assemble an apparatus for fractional distillation (see Fig. 20) and distil off the anhydrous hydrazine in a nitrogen stream at 112-114 °C.

Pour 2-3 ml of hydrazine on a watch glass and ignite it. The hydrazine should burn with a violet flame. If the sample of the obtained preparation does not ignite, freeze out the anhydrous hydrazine. To do this, put the receiver into a bath with ice. Pour the liquid off the precipitated crystals (what is the composition of the liquid and the crystals?), melt the crystals again, and repeat the operation.

Again ignite a small amount of hydrazine. Perform a number of reactions characterizing the properties of hydrazine. (Propose these reactions yourself.)

8. **Preparation of Hydroxylamine Chloride.** Dissolve 7 g of sodium hydroxide in 30 ml of water and saturate the solution with sulphur dioxide to an acid reaction, after which pass the stream of gas through the solution for another five minutes (*in a fume cupboard!*). Add the solution dropwise with continuous stirring to a solution containing 5.5 g of sodium nitrite in 9 ml of water cooled by a mixture of ice and salt. See that the temperature does not rise above 0 °C. Pour the solution into a round-bottomed flask, dilute it to a volume of 150 ml, and heat it to boiling on an electrical flask heater. Perform complete precipitation of the sulphate ions with a solution of barium chloride prepared by dissolving 37 g of barium chloride dihydrate in 45 ml of water.

Filter off the barium sulphate precipitate and evaporate the solution in a porcelain bowl first on a flame up to one-fourth of its initial volume, and then in a water bath until dry. Rapidly cool the hot bowl with cold water to facilitate the separation of the precipitate. Extract the hydroxylamine chloride from the solution, for which end transfer the triturated substance into a flask with a reflux condenser, pour in 30 ml of ethanol, and heat it on an electric stove with an enclosed heating element up to boiling. Pour off the liquid into a beaker and treat the solid substance again with 15 ml of ethanol. Combine the ethanol extracts, filter them through a crucible with a glass filtering bottom, and then evaporate the filtrate in a water bath up to the beginning of crystallization.

Filter off the precipitated crystals, collect them (*carefully, hydroxylamine is poisonous!*), weigh them, and calculate the yield in per cent. Examine the shape of the crystals under a microscope. Write the equations of the reactions.

9. **Preparation of Nitrogen(IV) Oxide and Nitrous Acid Anhydride.** Dry lead nitrate and quartz sand in a drying cabinet at 120 °C. Assemble an apparatus as shown in Fig. 86*a*. Put a mixture of 70 g of finely comminuted lead nitrate and 20 g of dry quartz sand into retort *1*. Fill columns *2* and *3* with phosphorus anhydride applied onto glass wool. Place thoroughly dried receiver *4* into a beaker with "dry ice". Heat the retort with a strong burner flame. Give attention to how the colour of the gas changes in liquefaction.

Assemble an apparatus for preparing nitrogen(II) oxide (Fig. 86*b*). Pour a concentrated solution of sulphuric acid into wash bottles *7*, and fill columns *8* with phosphoric anhydride applied onto glass wool. Dissolve 15 g of potassium nitrite and 7.5 g of potassium iodide in 75 ml of water. Pour the solution into flask *6*. Pour a 50% sulphuric acid solution into dropping funnel *5*.

After about 10 cm^3 of solid nitrogen(IV) oxide gathers in receiver

4, disconnect it from the apparatus (see Fig. 86*a*) without extracting it from the cooling mixture and connect it to offtake *9* of the apparatus for preparing nitrogen(II) oxide (nitrous acid anhydride) (see Fig. 86*b*). Prepare nitrogen(II) oxide by reacting sulphuric acid with an aqueous solution of a mixture of potassium nitrite and potassium iodide. Watch how the colour of the substance in receiver *4* changes when the nitrogen oxides react. Write the equations of the reactions.

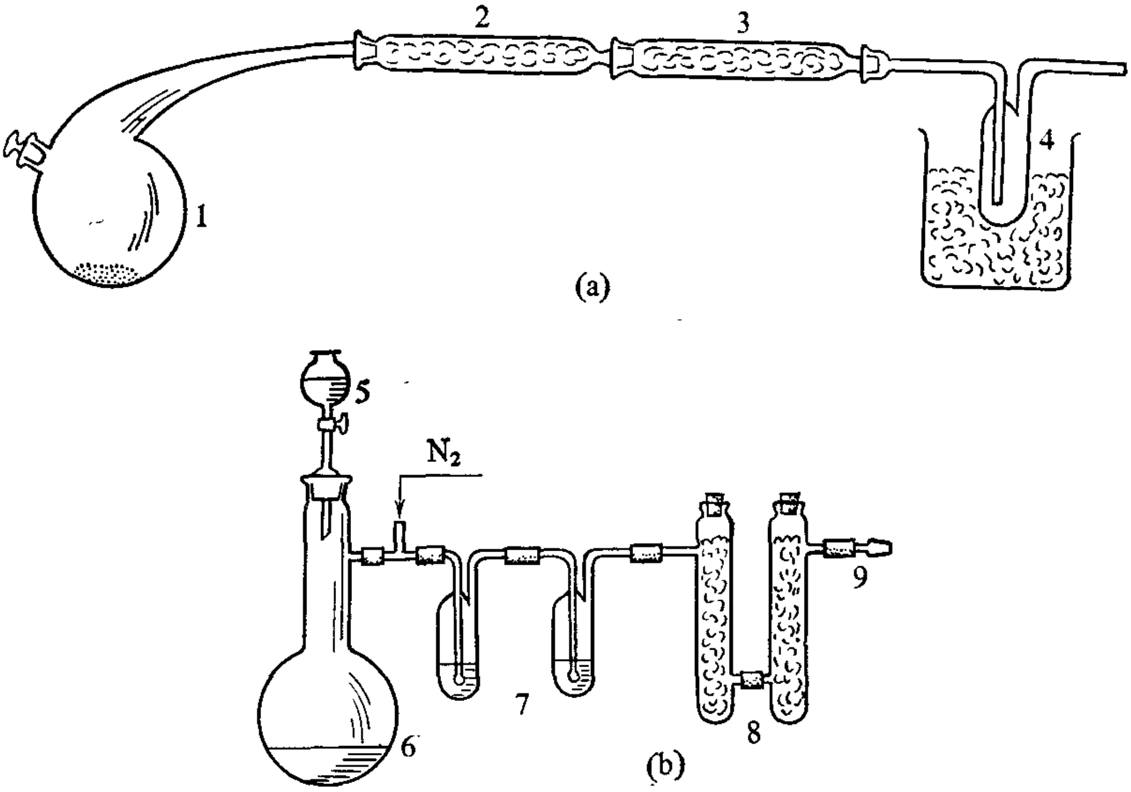


Fig. 86. Apparatus for preparing nitrogen(IV) oxide (*a*) and nitrogen(II) oxide (*b*)

Carry out reactions characterizing the properties of nitrogen(III) oxide.

10. Preparation of Nitrosyl Chloride by Reacting Nitrogen(II) Oxide with Chlorine in the Presence of an Activated Carbon Catalyst. Assemble an apparatus as shown in Fig. 87. Charge an apparatus for preparing dry chlorine and one for preparing dry nitrogen(II) oxide (see pp. 91 and 131) and connect them via a tee-piece to tube *1*. Put a layer of freshly calcined activated carbon into the tube (see "Preparation of Sulphuryl Chloride", p. 122). Move heating muffle *2* made from asbestos fastened with wire onto the tube. Thermometer *3* inserted into the muffle should lower to the surface of the tube. Immerse receiver *4* into a mixture of ice and sodium chloride. Displace the air from the apparatus with a stream of dry nitrogen(II) oxide and without stopping its flow, begin to pass chlorine through the apparatus, slightly heating (50 °C) with a gas burner flame the

place in the tube where the carbon is. What substance gathers in the receiver? Write the equation of the reaction.

Transfer one or two drops of the obtained liquid into a test tube containing a small amount of water. What forms in the solution? Hand in the prepared nitrosyl chloride to your instructor.

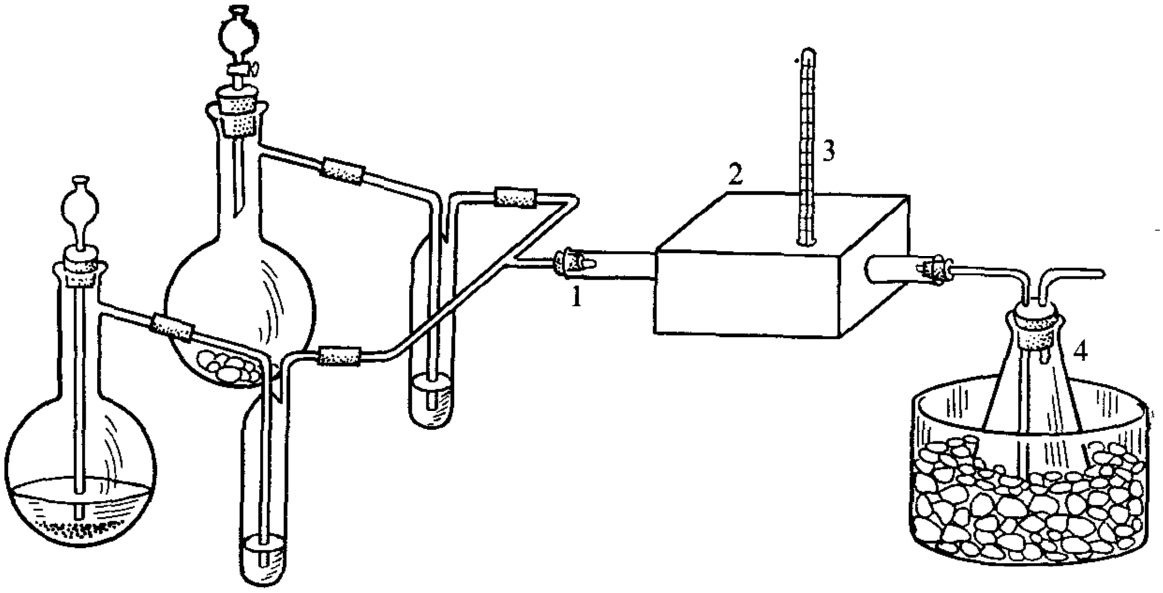


Fig. 87. Apparatus for preparing nitrosyl chloride

11. Preparation of Nitrosyl-Sulphuric Acid (Nitrosonium Bisulphate). Assemble an apparatus as shown in Fig. 88. Connect an apparatus for preparing dry sulphur dioxide (sulphurous acid anhydride) (see p. 113) to tube *4* for bubbling. Pour fuming nitric acid (see p. 133) into 250-ml three-neck flask *6* and cool it with a mixture of ice and salt. While vigorously mixing by means of mechanical mixer *1* having a seal (*2*, *3*) filled with concentrated sulphuric acid or vaseline oil, pass a stream of dry sulphur dioxide through the nitric acid up to the formation of a considerable amount of nitrosyl-sulphuric acid crystals. See that the temperature of the cooling mixture during the experiment does not rise above 0 °C.

When the reaction is completed, add 20 ml of glacial acetic acid and rapidly transfer the reaction mixture onto a filter No. 2 for filtration in an inert atmosphere (see Fig. 64*b*). Separate the nitrosyl-sulphuric acid crystals in an atmosphere of dry nitrogen, wash them on a filter with glacial acetic acid cooled to 5 °C, rapidly transfer them to a preliminarily weighed watch glass and put them in a vacuum desiccator over phosphoric anhydride. Dry them for two or three hours. Write the equation of the reaction. Weigh the dry crystals and calculate the yield in per cent.

12. Preparation of Nitrosyl Chloride by Reacting Nitrosyl-Sulphuric Acid with Sodium Chloride. Assemble an apparatus as shown in Fig. 89. Fill the system with dry nitrogen. Introduce into a flask

25 g of freshly prepared nitrosyl-sulphuric acid and 15 g of finely comminuted, dry sodium chloride preliminarily calcined in a crucible in a burner flame. Leave trap *2* empty, and place traps *3* and *4* in a cooling mixture of dry ice and acetone.

Heat flask *1* with the reaction mixture in a water bath. When the evolution of nitrosyl chloride from the reaction mixture terminates, close cock *5* and simultaneously extract the stopper from the flask. Next remove the water bath and also the cooling mixture from trap *3*. By heating trap *3* with your hand, distil off the nitrosyl chloride into trap *4*.

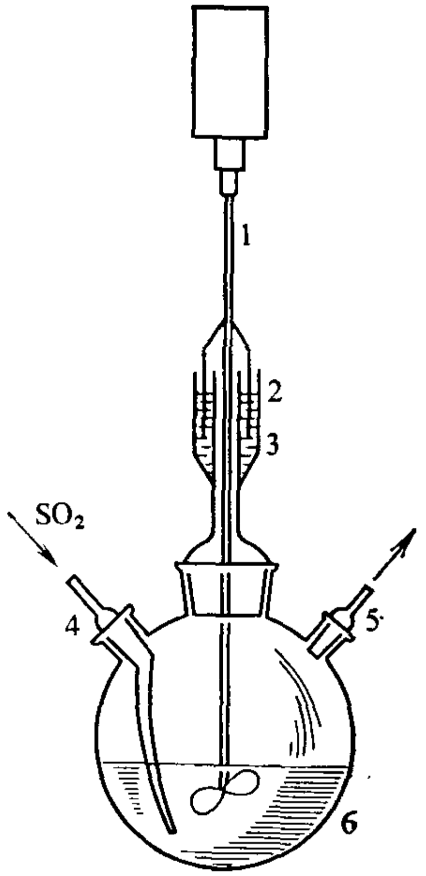


Fig. 88. Apparatus for preparing nitrosyl-sulphuric acid

Test how nitrosyl chloride interacts with water. What properties does the solution have? Write the equations of the reactions.

13. Preparation of Nitric Acid by Oxidizing Ammonia. Assemble an apparatus as shown in Fig. 90. Pour a 2% ammonia solution into flask *1*. Put a loose layer of freshly roasted platinized asbestos into the middle of tube *2* over a length of 4-5 cm. Pour a neutral litmus solution or several drops of methyl red into flask *3* and connect the short tube of this flask to water-jet pump *4*. Heat the platinized asbestos slightly with the flame of a gas burner and pass through it a very weak stream of a mixture of ammonia and air. How does the colour of the solution in flask *3* change? Write the equation of the reaction.

What processes are used in the chemical industry to manufacture nitric acid?

14. Preparation of Anhydrous Nitric Acid. Put 50 g of sodium nitrate into retort *1* made from refractory glass (see Fig. 80) and pour in 100 ml of a 98% solution of sulphuric acid. Carefully heat the retort with the flame of a burner and distil off a 90-95% nitric acid solution into receiver *4* cooled by a mixture of water and ice. Carry out distillation until the nitrogen oxides in the retort disappear.

Transfer the prepared fuming nitric acid into the flask of an apparatus for distillation in vacuum (Fig. 91). Coat all the ground-glass joints in the apparatus with moistened phosphoric anhydride or concentrated sulphuric acid. (*When pouring over the nitric acid, be ca-*

reful: *wear eye protection and work in a fume cupboard!*). Cool the flask containing the nitric acid with ice and introduce 100 ml of 98% sulphuric acid into it after cooling the latter to the same temperature (*carefully!*). Blow dry argon (nitrogen) through the appara-

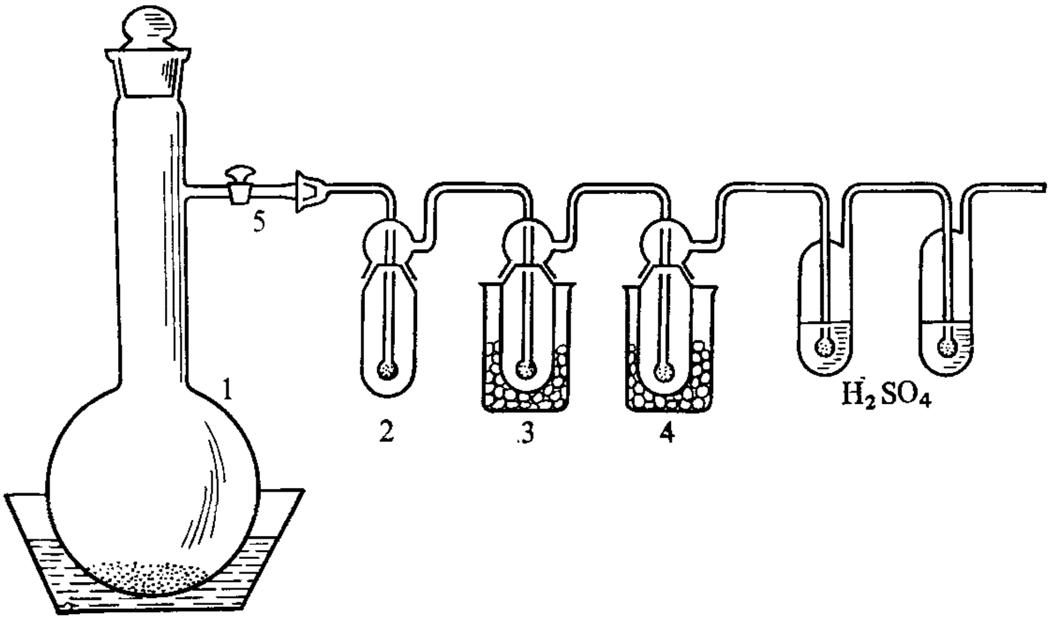


Fig. 89. Apparatus for preparing nitrosyl chloride

tus for 10-15 min, feeding in the gas through a capillary. Next connect the apparatus through a drying system and a safety bottle to a water-jet pump. Partly close the screw clamp on the capillary,

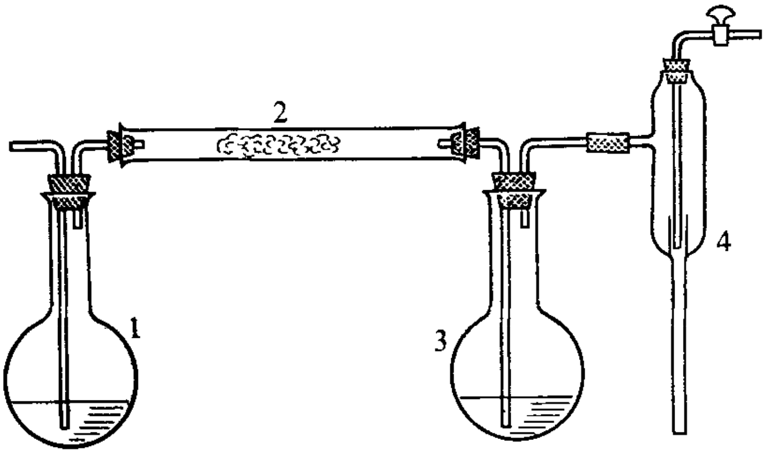


Fig. 90. Apparatus for oxidizing ammonia

retaining a weak stream of nitrogen. Heat the flask with the reaction mixture on a water bath. Collect the fraction boiling at 30-40 °C.

15. Preparation of Potassium Nitrite. Melt 1-2 g of potassium nitrate in a test tube and heat it above its melting point until oxygen bubbles stop evolving. Dissolve the cooled substance in water and add 1-2 ml of a dilute sulphuric acid solution. What happens?

Write the equations of the reactions. How can you prove that nitrous acid has formed in the solution?

What products form when potassium, copper, lead, or silver nitrates are roasted? What explains the different nature of their decomposition?

16. Preparation of Anhydrous Copper Nitrate. Prepare 7-10 ml of liquid nitrogen(IV) oxide (see Fig. 86*a*). If the oxide has solidified,

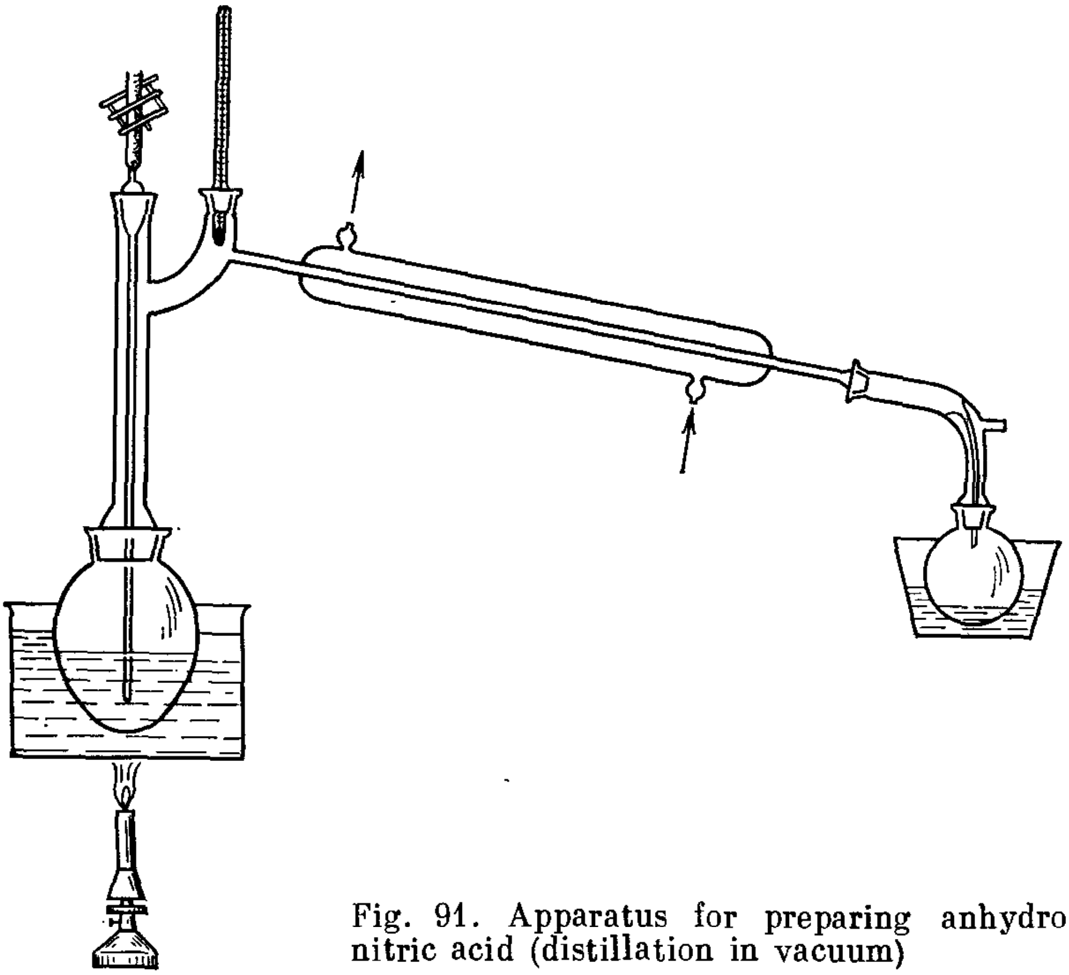


Fig. 91. Apparatus for preparing anhydrous nitric acid (distillation in vacuum)

carefully heat the receiver with your hands and pour the liquid through a funnel with a ground-glass joint into a test tube cooled by an ice-salt mixture (Fig. 92*a*) containing 15 ml of freshly distilled and thoroughly dried ethyl acetate. Add 3 g of finely cut up copper shavings to this mixture. Preliminarily wash the copper shavings with dilute hydrochloric acid and distilled water and dry them in a vacuum drying cabinet. Close the test tube containing the mixture with a stopper provided with a drying tube filled with phosphoric anhydride applied onto glass wool, and let it stand overnight in a fume cupboard.

After 10-12 hours, decant the solution from the unreacted copper shavings into vessel *1* (Fig. 92*b*). Connect the vessel via trap *2* and empty wash bottle *3* to a water-jet pump. Open clamps *4* and *5*,

switch on the water-jet pump, and then close clamp *5*. Place a water bath under vessel *1* and distil off the ethyl acetate and the nitrogen(IV) oxide in the vacuum produced by the water-jet pump.

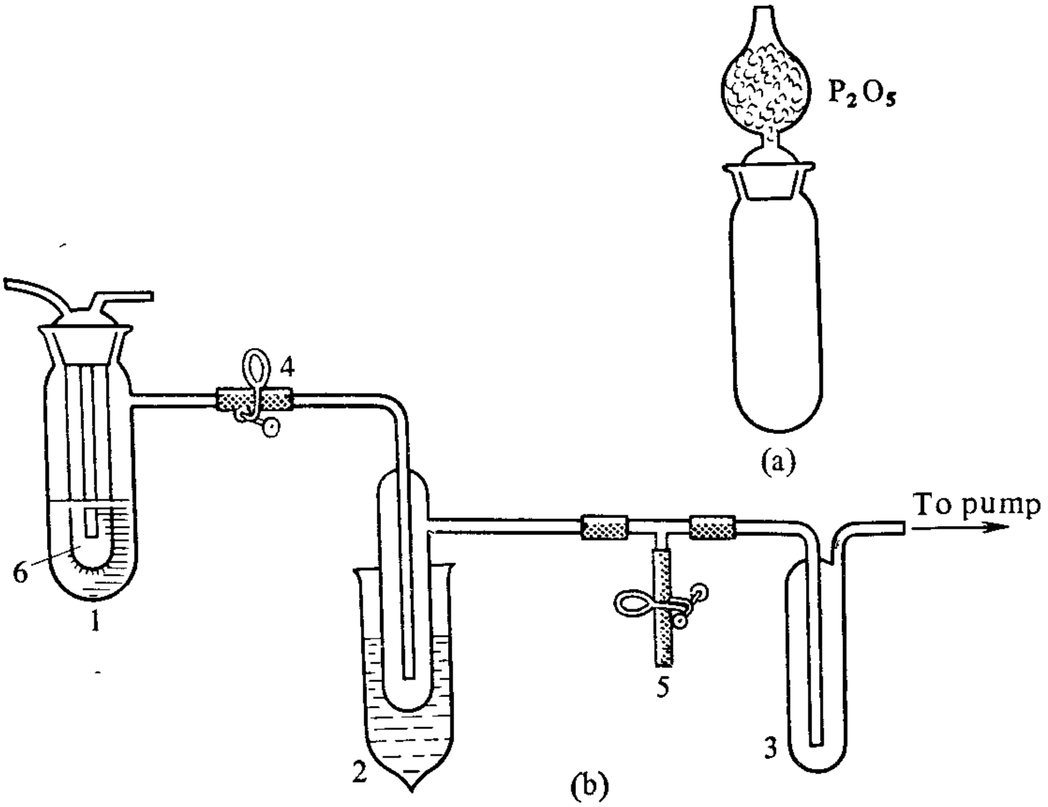


Fig. 92. Preparation of anhydrous copper nitrate: *a*—setup for reacting metallic copper with nitrogen(IV) oxide in ethyl acetate; *b*—apparatus for distilling off the solvent

When no liquid remains in vessel *1*, close clamp *4*, open clamp *5*, close the cock of the water-jet pump, and disconnect vessel *1*. In a dry chamber, extract the powdered anhydrous copper nitrate from the vessel and put it into a weighed weighing bottle. Calculate the yield in per cent.

14 PHOSPHORUS

Indicate the position of phosphorus in Mendeleev's periodic table of the elements, its electron configuration, the size of its atom, and its oxidation states.

Perform all experiments with white and red phosphorus, and also with hydrogen phosphide in a fume cupboard. White phosphorus is poisonous and readily ignites. Work with it requires special care. Handle white phosphorus only with pincers. Carry phosphorus to your workplace only in a porcelain bowl or in a mortar with water.

Burns produced by phosphorus are very dangerous! If white phosphorus gets on your skin, immediately remove it and wash the burnt spot with a 2% silver nitrate, copper sulphate, or potassium permanganate solution. After carrying out experiments with white or red phosphorus, immerse the laboratory ware for some time in a 10% copper sulphate solution, after which wash it in the usual way.

14.1 ALLOTROPY

Preparation of Red Phosphorus. (This experiment is prepared by one student who demonstrates it to the class.) Take a test tube with a drawn out end and fill it with carbon dioxide gas. Pour water heated to 30 °C into a mortar and lower a piece of white phosphorus into the water. Holding the phosphorus with pincers under the water, cut off a piece the size of a pea with a lancet or sharp knife. Rapidly dry the phosphorus with filter paper on a glass plate and lower it into the test tube filled with carbon dioxide.

Fig. 93. Arrangement for preparing red phosphorus

Heat the drawn out part of the test tube until the glass melts, shape its end into a hook, and seal the tube. Spill 8-10 g of naphthalene onto the bottom of a wide bulb-shaped test tube at least 40 cm long. Lower into it the sealed test tube containing the phosphorus and fasten the hook-shaped end of the tube with copper wire to a glass rod (Fig. 93). Cover the mouth of the wide test tube with a cardboard disk.

Fasten the wide tube in a stand and carefully heat it through asbestos gauze during three or four hours, seeing that the ampoule is constantly in naphthalene vapour.

Extract the sealed tube and see how the colour of the phosphorus changed.

Preparation of White Phosphorus. Put a small amount of dry red phosphorus on the bottom of a test tube and close its mouth with a piece of cotton wool. Secure the tube in a clamp of a stand and carefully heat the place where the phosphorus is (*in a fume cupboard!*). What happens? Observe the luminescence of the phosphorus in the dark.

What are the conditions for the transition of white phosphorus into the red modification and vice versa? What other allotropic modifications of phosphorus exist? How can they be prepared?

14.2 PROPERTIES

Flammability of Phosphorus. (*Perform the experiment in a fume cupboard!*). Put a small amount of dry red phosphorus on the edge of an iron plate placed on a ring of a stand and a small piece of white phosphorus on its other edge. Heat the plate with a burner closer to the edge where the red phosphorus is. What happens? Write the equation of the reaction.

Pour a small amount of copper sulphate, silver nitrate, and potassium manganate solutions into three beakers and drop a small piece of white phosphorus into each of them. In 10 or 15 minutes, extract the phosphorus from the solutions. Dry it as indicated above, put it on an iron plate, and heat it. What happens? How do the given salts affect white phosphorus? How can the different activity of white and red phosphorus be explained? Write the equations of the reactions.

Solubility of Phosphorus in Carbon Sulphide. This experiment is prepared by one student who demonstrates it to the class. (*Work in a fume cupboard, extinguish all burners!*) Pour 2-3 ml of carbon sulphide into a small porcelain bowl and lower a small piece of white phosphorus into it. What occurs? Take a small sheet of filter paper with pincers, wet it with the solution of phosphorus in carbon sulphide, and see what happens. Test the solubility of red phosphorus in carbon sulphide.

How is phosphorus produced from its natural compounds?

14.3 COMPOUNDS

HYDROGEN PHOSPHIDE

Pour water acidified with hydrochloric acid into a beaker and throw several small pieces of calcium phosphide into it. What happens? Write the equation of the reaction. How can you explain the ignition of the evolved gas?

What compounds of phosphorus with hydrogen do you know? Compare the properties of phosphine and ammonia.

PHOSPHOROUS ANHYDRIDE AND PHOSPHOROUS ACID

Preparation. Assemble an apparatus as shown in Fig. 94. Pour a small amount of vaseline oil into wash bottle *1*. Fill U-tube *2* with small pieces of roasted calcium chloride. Put three small pieces

of white phosphorus into porcelain boat *3*. Place the boat with the phosphorus into refractory glass tube *4* nearer to its left opening. Connect two U-tubes *5* and *6* intended for receiving the prepared substance to a water-jet pump. Remove the right stopper from tube *4* and ignite the phosphorus by touching it with a heated glass rod.

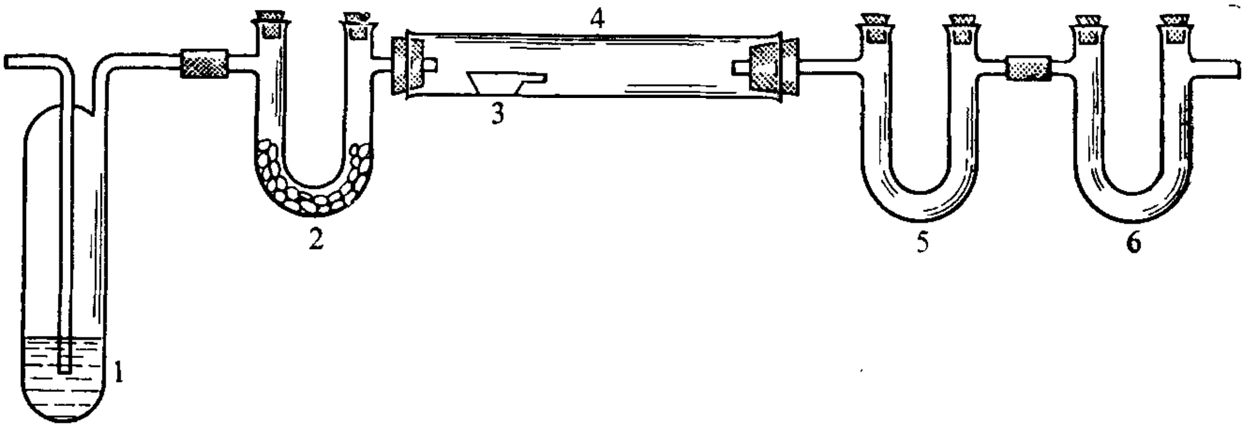


Fig. 94. Apparatus for preparing phosphorous anhydride

Replace the stopper and switch on the water-jet pump (very slow operation). When the entire phosphorus has reacted, disconnect the pump and dissolve the phosphorous anhydride gathered in tube *4* and U-tubes *5* and *6* in 10-20 ml of distilled water. Filter the solution through a paper filter and keep it for further experiments.

What is the basicity of phosphorous acid? Write the coordination formula of phosphorous acid. What coordination number does phosphorus exhibit in its compounds?

Properties of Phosphorous Acid. Divide the phosphorous acid solution into three parts. Neutralize the first part with soda up to a weakly acidic reaction and test it with a silver nitrate solution. What do you observe? Heat the liquid with the precipitate. What occurs?

Add several drops of a dilute potassium permanganate solution to the second part of the solution. What happens? Write the equations of the reactions.

Put the third part of the phosphorous acid solution into a porcelain bowl and evaporate it first in a water bath, and then carefully heat it in a sand bath. What is observed? Write the equation of the reaction. What properties of phosphorous acid are indicated by the above three reactions?

PHOSPHORIC ANHYDRIDE

Assemble an apparatus as shown in Fig. 95. Thoroughly dry all parts of the apparatus prior to the experiment. What should the calcium chloride tube be filled with? Connect the wash bottle (or a U-tube) to the water-jet pump. Put red phosphorus into a spoon

for burning, ignite it with the flame of a burner, and introduce it into the three-neck bottle. Switch on the water-jet pump and pass a stream of dry air through the apparatus.

Repeat the phosphorus burning operation several times. Rapidly spill out the substance that has settled in the three-neck and wash

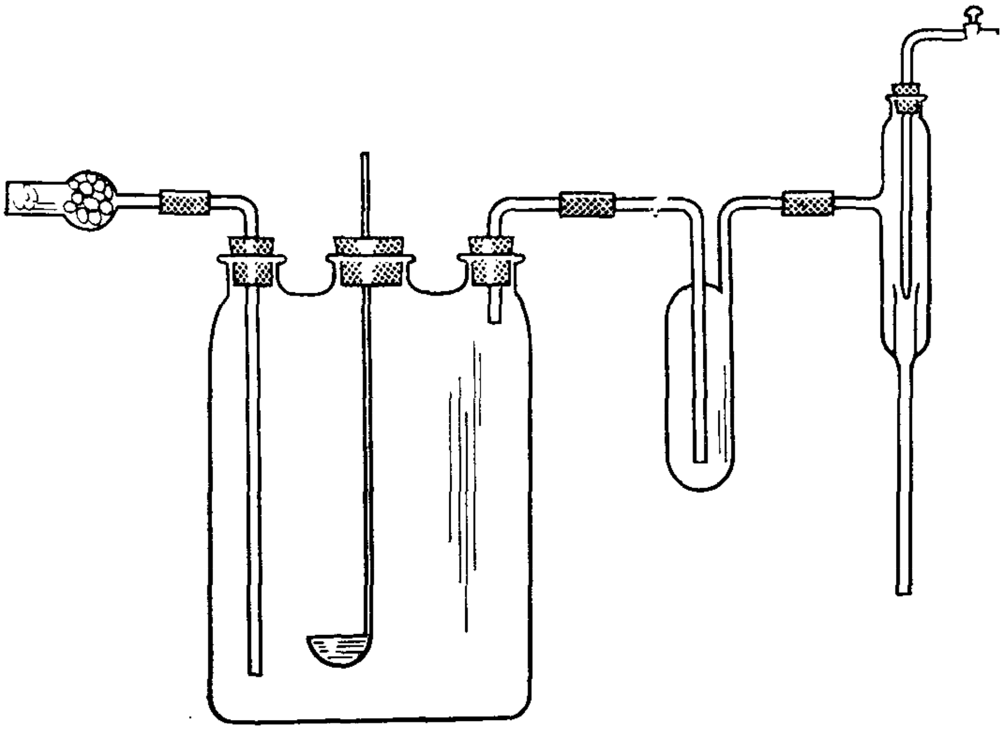


Fig. 95. Apparatus for preparing phosphoric anhydride

bottles into a dry weighing bottle and close it with its lid. Write the equation of the reaction.

Spill a part of the preparation into a porcelain bowl and let it stand to the end of the lesson. Introduce the other part in small portions into a bowl with water. What happens? Test the solution with litmus paper. Write the equations of the reactions.

What is the structure of a phosphoric anhydride molecule?

PHOSPHORIC ACIDS

Write the formulas of the following phosphoric acids: metaphosphoric, pyrophosphoric, and orthophosphoric. Acquaint yourself with their appearance.

Metaphosphoric Acid. *Reactions for Determining Metaphosphoric Acid and Its Salts.* 1. Pour about 1 ml of an aqueous protein solution into a test tube and add to it approximately the same amount of a sodium metaphosphate solution acidified with acetic acid. What do you observe? See whether the protein solution is affected in the same way by sodium metaphosphate and acetic acid solutions taken separately.

2. Pour a few drops of silver nitrate into a sodium metaphosphate solution. Note the colour of the precipitate. See how it reacts with dilute nitric acid. Write the equations of the reactions. In what medium can silver metaphosphate be precipitated?

Preparation of Metaphosphoric Acid. **1.** Dissolve 0.1 g of phosphoric anhydride in water and test the solution with an aqueous protein solution. What do you observe?

2. Put 1-2 ml of a 95% orthophosphoric acid solution into a porcelain bowl. Heat it on a sand bath until it acquires a syrupy consistence, after which roast it at 350 °C. How can you prove that metaphosphoric acid has been obtained? Write the equation of the reaction.

Orthophosphoric Acid. *Reaction for Determining Orthophosphoric Acid and Its Salts.* **1.** Pour "molybdenum liquid"* into a solution of sodium hydrogen phosphate or phosphoric acid. What is the composition of the precipitate? Write the equation of the reaction. Does the precipitate dissolve in nitric acid?

2. See how silver nitrate reacts with a solution of sodium orthophosphate. Note the colour of the precipitate. Write the equation of the reaction. Does the substance dissolve in a 1 *N* nitric acid solution?

Preparation of Orthophosphoric Acid. **1.** Dissolve a small amount of phosphoric anhydride in distilled water, add several drops of dilute sulphuric acid, and boil the solution. Treat the solution with molybdenum liquid. Explain what happens.

2. Put a little phosphorite into a test tube, pour a 50% sulphuric acid solution onto it, and heat up to boiling. Pour the solution off the precipitate, dilute it with water, and add molybdenum liquid to it. What occurs? Write the equations of the reactions.

3. Put 0.2 g of red phosphorus into a small flask and add 10-15 ml of a concentrated nitric acid solution in small portions (*in a fume cupboard!*). Put the flask in a water bath and heat it until the reaction terminates. Pour the solution into a porcelain bowl and evaporate the excess nitric acid in a water bath. How can you prove that the residue is orthophosphoric acid?

Pyrophosphoric Acid. *Reactions for Determining Pyrophosphoric Acid and Its Salts.* **1.** Test the action of a pyrophosphoric acid on a protein. What is observed?

2. Add several drops of a silver nitrate solution to 2-3 ml of a sodium dihydropyrophosphate solution. What is observed? Does

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* To prepare "molybdenum liquid" for determining the phosphate ion, dissolve 50 g of ammonium sulphate in 450 ml of a 68% nitric acid solution and 150 g of ammonium molybdate in 400 ml of distilled water. Cool the second solution to room temperature and pour it into the first one with constant stirring. Bring the total volume of the solution up to one litre. In a few days, filter off the solution for the precipitate.

the substance obtained dissolve in a dilute nitric acid solution? Write the equations of the reactions.

Preparation. Put 3 ml of concentrated orthophosphoric acid into a porcelain bowl. Heat it on a sand bath until the liquid acquires a syrupy consistence, and then heat it up to 240 °C. How can you prove that the substance obtained is pyrophosphoric acid?

SALTS OF PHOSPHORIC ACIDS

Hydrolysis of Ortho- and Pyrophosphoric Acid Salts. Use a universal indicator to determine the pH of a solution of mono-, di-, and trisubstituted sodium salts of orthophosphoric acid, and also of di- and tetrasubstituted sodium salts of pyrophosphoric acid. Write the equations of the reactions and explain why a different medium is obtained when the given salts are dissolved in water.

Calcium Salts of Orthophosphoric Acid. Pour a calcium chloride solution into three test tubes. Add ammonia and a sodium hydrogen phosphate solution to one of them, only a sodium hydrogen phosphate solution to the second one, and a sodium dihydrogen phosphate solution to the third one. What do you observe? Write the equations of the reactions and explain how the medium affects the course of the process.

Test how the prepared precipitates react with acetic or hydrochloric acids. Explain the observed phenomena. What is the composition of phosphorite, precipitate, superphosphate, and double superphosphate? What are the conditions for their use in agriculture?

Thermal Decomposition of Orthophosphates. Roast several crystals of monosubstituted sodium orthophosphate on the lid of a crucible. Continue the decomposition reaction until it terminates (how can this be determined?). Cool the product of roasting, dissolve it in water, and determine the salt of what phosphoric acid is in the solution. Write the equation of the reaction.

What products form when disubstituted sodium and ammonium-sodium orthophosphates are roasted? What orthophosphates are used as fertilizers? Compare the strength of the oxyacids of phosphorus, sulphur, and chlorine, and also of nitrogen and phosphorus.

PHOSPHORUS HALIDES

Preparation of Phosphorus Trichloride and Pentachloride. (*This experiment is performed* by two students *in a fume cupboard!*) Assemble an apparatus as shown in Fig. 96. Put 0.2 g of dry red phosphorus into each of Wurtz test tubes *1* and *2*. See that the lower ends of gas-discharge tubes *3* feeding chlorine into reaction tubes *1* and *2* are 2-3 cm above the phosphorus layer. Displace air from the apparatus using dry carbon dioxide gas, and then fill it with dry chlorine

(what must be poured into the wash bottles?). Carefully heat the phosphorus in both test tubes with the flame of a gas burner. What do you observe? By regulating the heating and the rate of flow of the chlorine with the aid of clamps, obtain phosphorus trichloride* in one receiver and phosphorus pentachloride in the other.

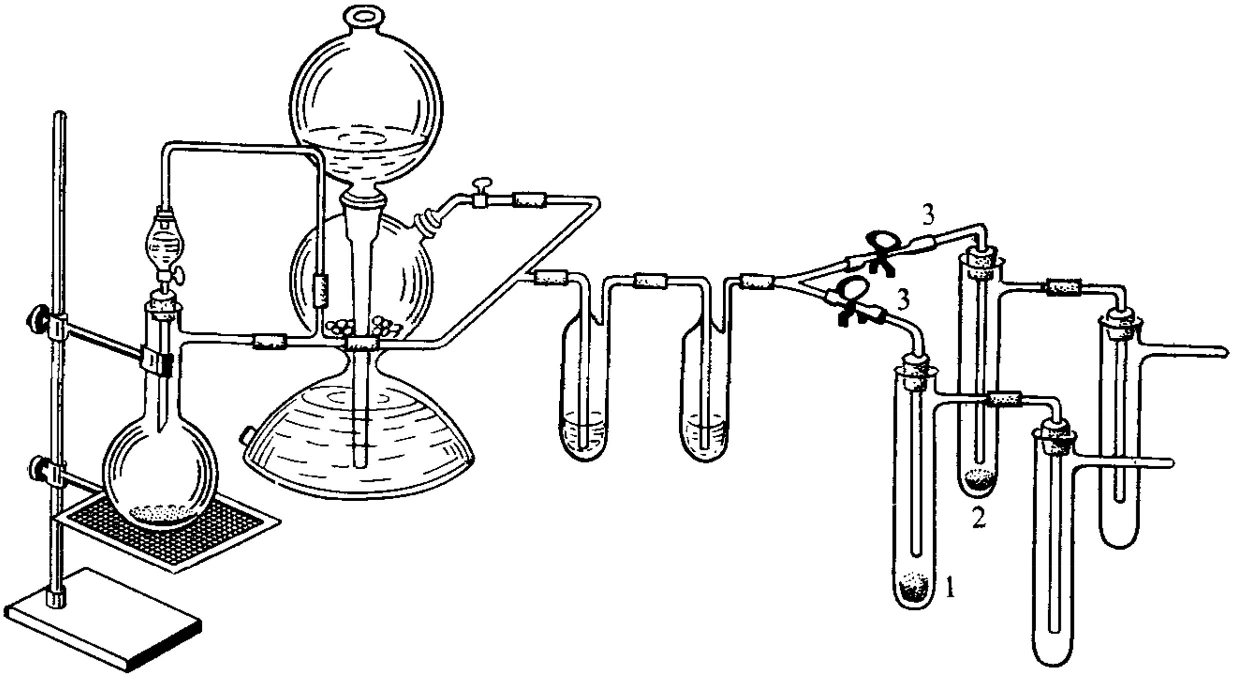

Fig. 96. Apparatus for preparing phosphorus chlorides

Write the equations of the reactions. When the process is completed, displace the chlorine from the apparatus with carbon dioxide. Disconnect the receivers with the prepared substances and thoroughly close them.

Hydrolysis of Phosphorus Trichloride. Pour 3 ml of distilled water into a test tube and add a small amount of phosphorus trichloride dropwise. What do you observe? Write the equation of the hydrolysis reaction. Determine the composition of the hydrolysis products.

Enter the boiling and melting points of the phosphorus halides in your laboratory notebook in the form of a table. Compare these constants and explain the law according to which they change.

Hydrolysis of Phosphorus Pentachloride. Introduce a small amount of the prepared phosphorus pentachloride into distilled water. What do you observe? Write the equation of the reaction and establish the composition of the products formed when phosphorus pentachloride reacts with water.

What class of compounds do the phosphorus halides belong to?

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* Phosphorus trichloride can also be prepared by carefully heating a mixture of phosphorus pentachloride with red phosphorus taken in stoichiometric amounts. Put the reaction mixture into a Wurtz test tube and distil off the formed phosphorus trichloride into a receiver.

SUPPLEMENTARY EXPERIMENTS AND SYNTHESES

1. Burning of Phosphorus under Water. *Perform the experiment in the presence of your instructor!* Pour 10-15 ml of distilled water into a wide test tube, secure it in a clamp of a stand, and immerse it into a beaker with water. Drop a very small piece of white phosphorus into the test tube with water and heat the water in the beaker to a temperature 30-40 °C above the melting point of white phosphorus. Regulate the flow of oxygen from a gas meter so that you can count the individual bubbles and introduce a glass gas-discharge tube from the gas meter bent at right angles into the test tube so that the bubbles of the evolving oxygen come into contact with the molten phosphorus. What is observed?

2. Preparation of Hydrogen Phosphide. *(Perform the experiment in a fume cupboard!)* Assemble an apparatus for preparing hydrogen phosphide (see Fig. 47). Pour 40 ml of a 30% potassium hydroxide solution into a 100-ml round-bottomed flask, introduce 1-2 g of white phosphorus into it, and add 2-3 ml of ethyl ether (what is the ether poured in for?). Close the flask with a stopper accommodating a gas-discharge tube. Immerse the free end of this tube into a bath with water. Heat the contents of the flask first carefully, and then strongly to the boiling point of the liquid. What do you observe? When the reaction has ended, remove the burner and lower the glass window of the fume cupboard. Write the equation of the reaction.

What compounds of phosphorus with hydrogen are known? Compare the properties of phosphine (hydrogen phosphide) and ammonia. Write the coordination formulas of the phosphonium ion and hypophosphorous acid.

3. Preparation of Phosphonium Iodide. (*Perform the experiment in a medium of dry carbon disulphide. Carbon disulphide is poisonous and readily ignites, its mixture with air is explosive. Work with it requires great care and attention. Distil carbon disulphide in a water bath in the absence of an open flame!*)

After performing the synthesis, treat the remaining carbon disulphide and the ware in which various operations were carried out with an abundant amount of an alkaline potassium permanganate solution. Continue the treatment until the oily drops of the carbon disulphide disappear from the surface of the solution. (*Perform all the operations in a fume cupboard!*)

To dry carbon disulphide, separate it from the water in which it is stored (*carbon disulphide is stored under water!*) with the aid of a separatory funnel. Pour the carbon disulphide into a bottle with a ground-glass stopper. Spill such an amount of fused calcium chloride into the bottle that its entire bottom is covered with the desiccant, and dry the carbon disulphide at least 24 hours.

Pour the dry carbon disulphide into a flask for distillation under atmospheric pressure (see Fig. 20) and distil it over the fused calcium chloride, collecting the fraction boiling at 45-46 °C. Heat with hot water in the absence of heating equipment.

Assemble an apparatus as shown in Fig. 97. Dissolve 10 g of commercial white phosphorus in 50 ml of dry carbon disulphide in flask *1*. Pass a stream of dry carbon dioxide gas through the apparatus.

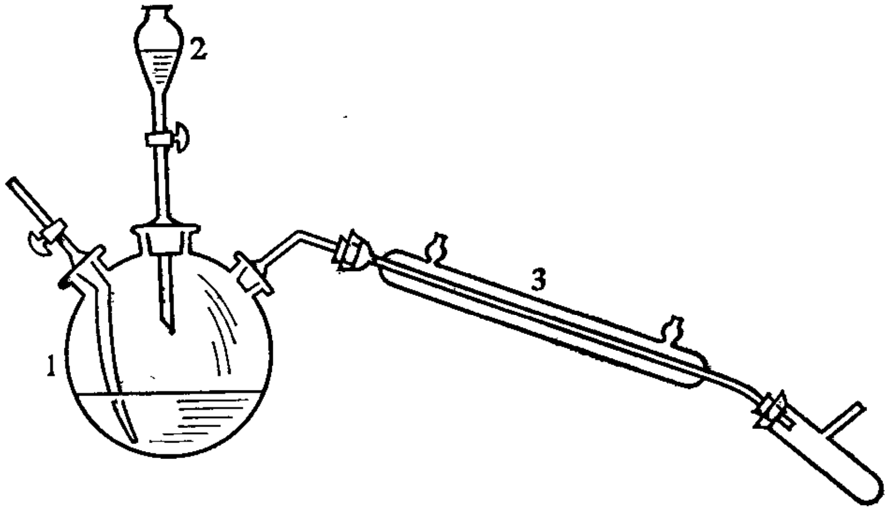


Fig. 97. Apparatus for preparing phosphonium iodide

Remove dropping funnel *2* and introduce 17.5 g of commercial iodine through the middle opening of the flask in small portions. Cool the flask with ice. After introducing all the iodine, insert the dropping funnel, remove the cooling, and distil off all the carbon disulphide (*in a water bath*) in a stream of carbon dioxide.

Replace the cooler with an adapter and connect a new dry, previously weighed receiver to it with the aid of a ground-glass joint. Use as the receiver a drawn out Wurtz test tube whose side arm is provided with a calcium chloride tube filled with phosphoric anhydride on glass wool.

Pour in 5 ml of water dropwise from the dropping funnel, after which heat flask *1* on a water bath to 80-90 °C. Distil off the phosphonium iodide into a receiver. Repeat the hydrolysis operation several times until phosphonium iodide stops evolving.

Transfer the phosphonium iodide crystals deposited on the adapter walls into the receiver by carefully heating the adapter with a weak burner flame. Seal the Wurtz test tube (*wear eye protection!*). Weigh the ampoule and the remaining part of the test tube. Calculate the yield in per cent. Write the equations of the reactions.

4. Preparation of Hypophosphorous Acid. (*Perform the experiment in a fume cupboard!*) Assemble an apparatus as shown in Fig. 98. Prepare a suspension of 12 g of barium hydroxide in 150 ml of water

in four-neck flask *1*. Place 2 g of white phosphorus into test tube *2*. Blow argon through flask *1* via tube *4* during 30 min. Switch on the agitator, turn test tube *2* in its ground-glass joint, and introduce the phosphorus into the barium hydroxide suspension. Heat the reaction flask with the flame of a burner until phosphine stops evolving (how can this be determined?). Next cool the flask.

Pass carbon dioxide through the reaction mixture during 15 min (connect a Kipp gas generator to tube *4*). Filter the precipitate (what is its composition?) on a Büchner funnel and wash it with several portions of hot water (50-60°C). Evaporate the filtrate together with the washing water in a porcelain bowl in a water bath up to one-third of the initial volume, again filter the solution through a smooth filter, and once more evaporate it up to the appearance of a crystalline film (*be careful, avoid overheating!*). Add an equal volume of ethanol to the warm solution. Cool the mixture and separate the crystals by filtration. Write the equations of the reactions.

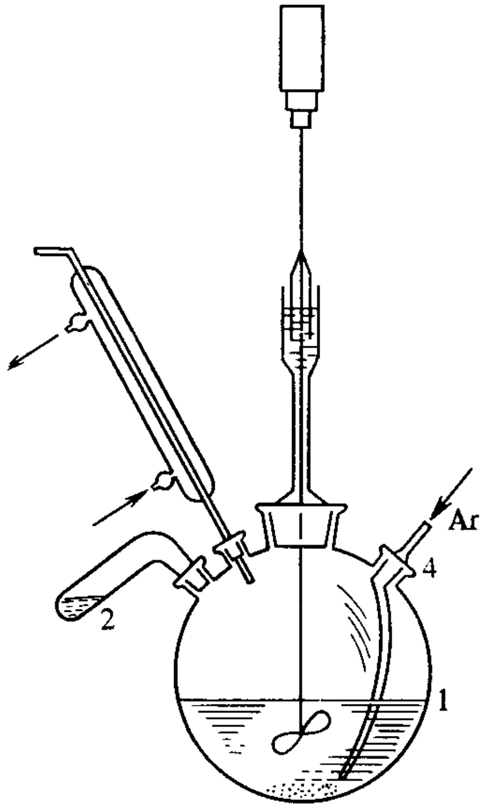


Fig. 98. Apparatus for preparing hypophosphorous acid

Treat the unreacted white phosphorus deposit remaining on the walls of the reaction flask with bromine water.

To prepare hypophosphorous acid, dissolve 4 g of freshly prepared barium hypophosphite monohydrate in 60 ml of water in a glass beaker. Introduce 5 ml of a 25% sulphuric acid solution into the solution while stirring it. Let the mixture stand overnight.

Decant the solution and filter it with suction through a dense paper filter into a dry and clean Bunsen flask. Carefully evaporate the filtrate on a sand bath (*in a fume cupboard!*) until the temperature of the solution rises to 105-110 °C (*a thermometer!*). See that the liquid does not boil and does not ignite. Cool the bowl in an ice and water mixture for 20-30 min. Filter off the crystals in a stream of nitrogen (see Fig. 64*b*) using a glass filter No. 2. Conduct reactions characterizing the properties of hypophosphorous acid.

5. Preparation and Separation of Phosphorus Tri- and Pentachlorides. *Preparation of Phosphorus Trichloride.* (*Perform the experiment in a fume cupboard!*) Wash 15 g of commercial red phosphorus with

a dilute sodium hydroxide solution. Filter on a Büchner funnel and dry in a vacuum drying cabinet at 70-80 °C.

Assemble an apparatus as shown in Fig. 99*a*. Put 10 g of purified dry phosphorus into test tube *1*. Cool test tube *2* with ice. Displace the air from the apparatus with a stream of dry nitrogen (carbon dioxide). Pass a stream of dry chlorine through the apparatus, heating tube *1* in a sand bath up to a temperature of 250-300 °C (*use a thermometer!*). Carry out chlorination so that the formed phosphorus

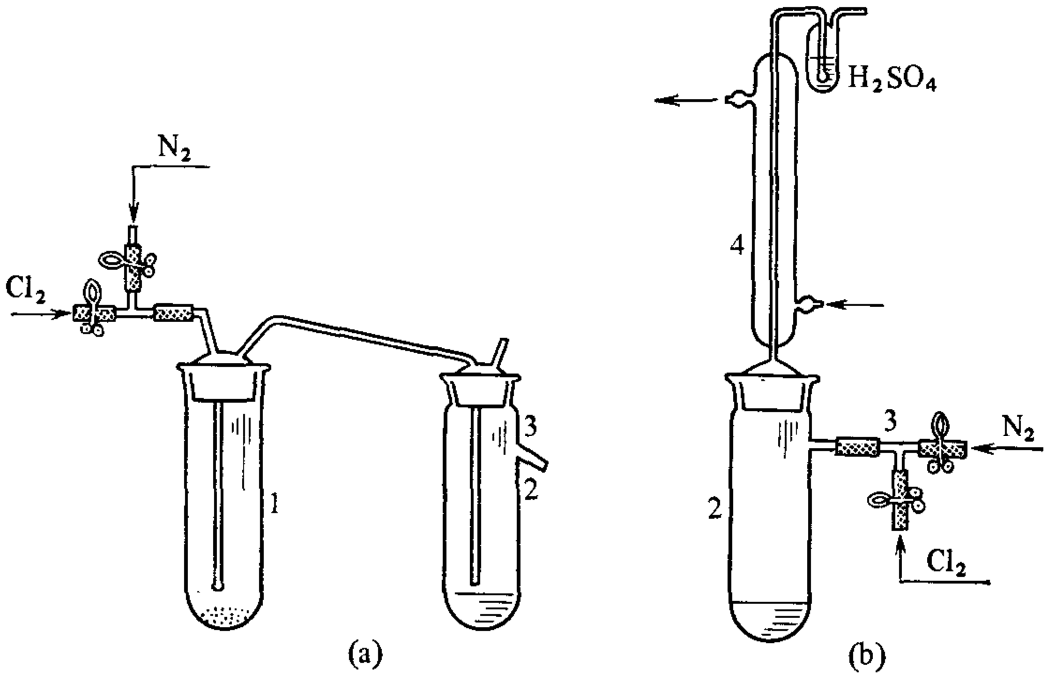


Fig. 99. Apparatuses for chlorinating phosphorus (*a*) and preparing phosphorus pentachloride (*b*)

trichloride is uniformly distilled off into receiver *2*. Terminate the chlorination when about one-fourth of the taken amount of phosphorus remains in tube *1*.

Purify the "crude" phosphorus trichloride. Put 1.5-2 g of dry red phosphorus into test tube *2*. Connect the latter to a dephlegmator with a thermometer and a cooler provided with a receiver (see Fig. 20) via a standard ground-glass joint. Fill the apparatus with dry nitrogen (carbon dioxide) through side arm *3* and distil the phosphorus trichloride in a stream of nitrogen, heating the test tube with the flame of a burner. Collect the fraction boiling within the temperature interval 75-77 °C. Pour the prepared phosphorus trichloride into a dry drawn out test tube. Seal the latter (*wear eye protection!*). Hand in the ampoule with the substance to your instructor.

Preparation of Phosphorus Pentachloride. Prepare phosphorus trichloride or take the substance from the laboratory assistant. Assemble an apparatus as shown in Fig. 99*b*. Put the phosphorus trichloride into test tube *2* and connect reflux condenser *4* with water cooling to

tube *2*. Displace the air from the apparatus with a stream of dry nitrogen through side arm *3* and then pass a stream of dry chlorine through the apparatus while heating test tube *2* in a water bath. Perform chlorination until all the liquid transforms into white crystals of phosphorus pentachloride. Transfer the substance into a drawn out test tube in a dry chamber. Seal the latter (*wear eye protection!*). Hand in the ampoule with the substance to your instructor.

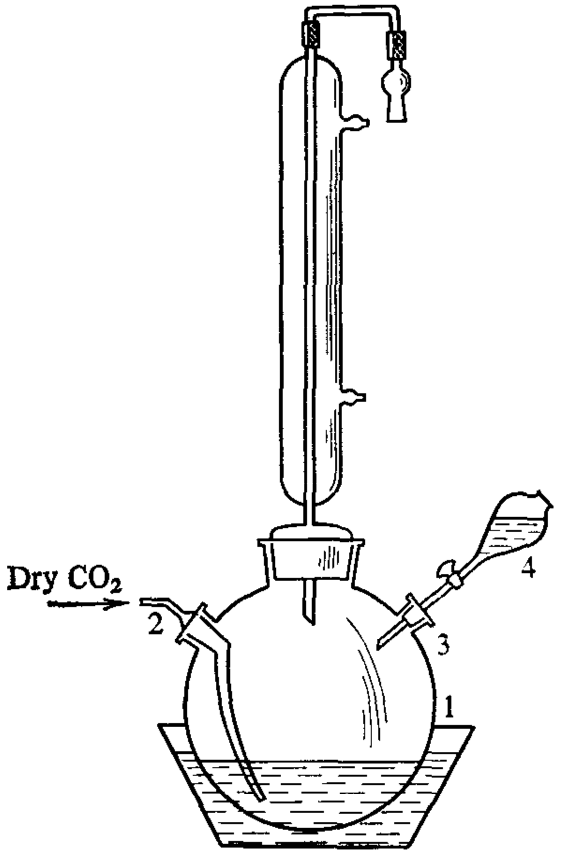


Fig. 100. Setup for preparing phosphorus tribromide from white phosphorus

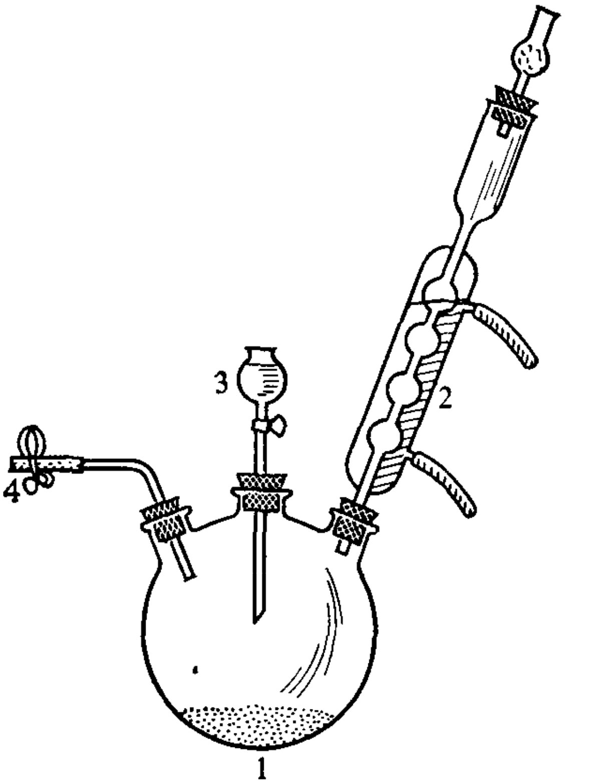


Fig. 101. Setup for preparing phosphorus tribromide from red phosphorus

6. Preparation of Phosphorus Tribromide by Reacting White Phosphorus with Bromine. (*Perform the experiment in a fume cupboard!*) To prepare phosphorus tribromide, one must have purified white phosphorus and dry bromine.

To prepare pure white phosphorus, place commercial white phosphorus into a wide test tube with water. Heat the tube with the phosphorus in a beaker with hot water until the phosphorus melts. Vigorously stir the melt with a glass rod during 20-25 min. Stir it until the "dirt" gathers on the surface of the melt and the latter becomes transparent.

Cool the test tube in the air. Put the tube with the solidified phosphorus into a crystallizer with water. Break the tube under the water and remove the dirty surface layer from the obtained piece

of phosphorus with a sharp knife under the water. Transfer the pure phosphorus into a bottle with water.

Carefully pour bromine (*in a fume cupboard, lower the glass window!*) into the crystallizer with water and the remaining phosphorus. "Slake" the phosphorus with bromine water while stirring with a glass rod.

Assemble a setup as shown in Fig. 100. Lubricate the ground-glass joints with phosphoric acid. Displace the air from the setup with dry carbon dioxide. Pour 50 ml of absolute benzene into 250-ml

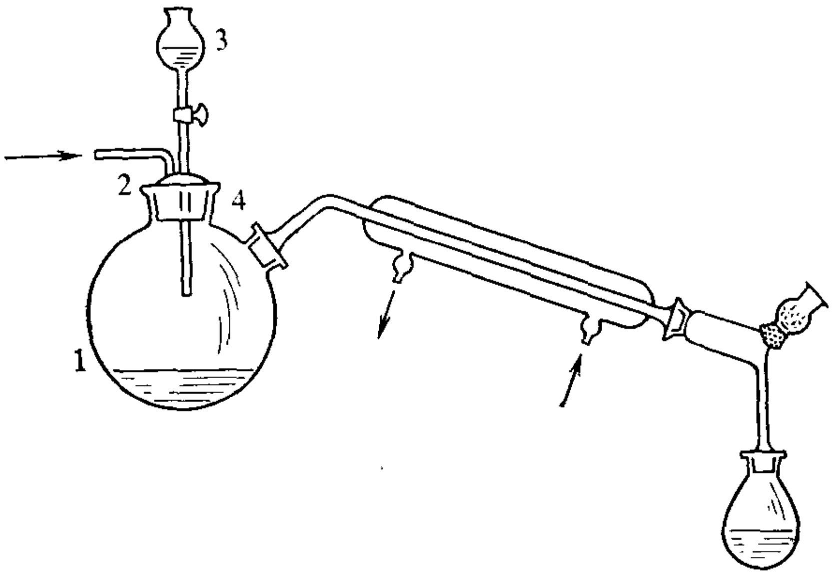


Fig. 102. Apparatus for preparing phosphorus iodide

flask *1*. Take the phosphorus with pincers from the bottle with water and transfer it into a mortar with water. Cut off several pieces of the phosphorus under the water and weigh about 8 g in a small beaker with water. Rapidly dry each piece with filter paper, and then lower it in turn into small beakers with absolute ethanol and absolute ether. Remove dropping funnel *4* and carefully introduce 8 g of the pure white phosphorus into the flask via opening *3*.

Replace the dropping funnel and pour 20 ml of dry bromine into it (*wear gloves!*). Place a bath with cold water under the flask. Add the taken amount of bromine dropwise from the dropping funnel into the reaction flask during 20-25 min.

When the reaction ends, rapidly transfer the product into an apparatus for fractional distillation at atmospheric pressure (see Fig. 20). Distil off the benzene at 80 °C, heating the flask on an electric stove with an enclosed coil. After distilling off the benzene, pour the water out of the cooler. Disconnect the receiver with the benzene and connect a new dry receiver. Perform further distillation and gather the fraction boiling at 172-174 °C.

Rapidly pour over the substance into a weighed drawn out test tube. Seal the latter (*wear eye protection!*). Weigh the ampoule with

the substance and the remaining parts of the tube. Write the equation of the reaction. Calculate the yield in per cent.

7. Preparation of Phosphorus Tribromide by Reacting Red Phosphorus with Bromine. (*Perform the experiment in a fume cupboard!*) Assemble an apparatus as shown in Fig. 101. Put 4 g of dry red phosphorus into three-neck round-bottomed flask *1*. Fill cooler *2* with water. Displace the air from the setup with a stream of dry carbon dioxide and close tube *4* feeding in the gas with a clamp. Pour dry bromine in dropwise from dropping funnel *3*. What amount of bromine should be poured into the funnel? Agitate the flask during the experiment. What deposits on the walls of the flask? Stop the reaction when a small amount of the unreacted phosphorus remains. Remove cooler *2* and close the opening with a stopper.

Replace the dropping funnel with a dephlegmator provided with a thermometer and a Liebig condenser (see Fig. 20). Carefully heat the flask with the flame of a gas burner. What happens? Collect the fraction boiling at 172-174 °C. Transfer the prepared phosphorus tribromide into a weighed drawn out test tube and seal it (*wear eye protection!*). Weigh the ampoule together with the remaining parts of the test tube. Calculate the yield in per cent.

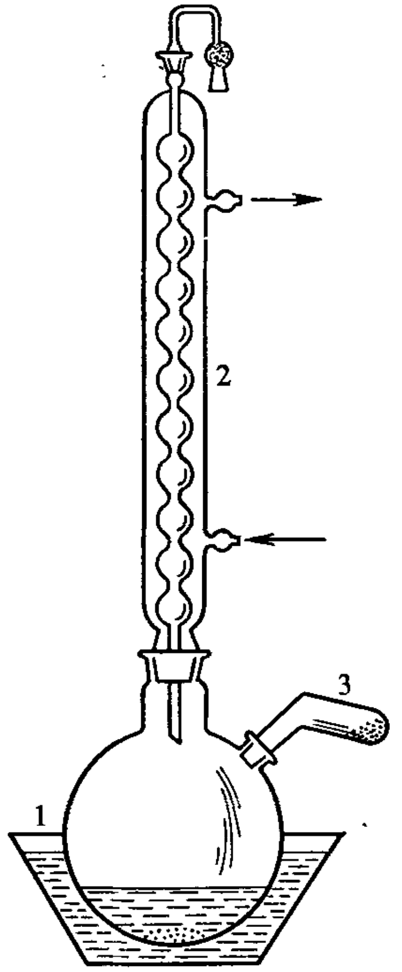


Fig. 103. Setup for preparing phosphorus thiochloride

8. Preparation of Phosphorus Iodide P_2I_4. To prepare phosphorus iodide, one must have thoroughly dried carbon disulphide (see "Preparation of Phosphonium Iodide") and purified white phosphorus (see "Preparation of Phosphorus Tribromide"). (*Perform the experiment in a fume cupboard!*).

Assemble an apparatus as shown in Fig. 102. Lubricate the ground-glass joints with phosphoric acid. Fill the apparatus with dry carbon dioxide using offtake *2*. Pour 10 ml of dry carbon disulphide from dropping funnel *3* into flask *1*.

Cut off 1 g of white phosphorus under water, dry it with filter paper, and wash it with absolute ethanol and absolute ether. Introduce the phosphorus into flask *1* through opening *4* and attach the cooler.

Dissolve 8.2 g of iodine (freshly sublimed) in 40 ml of carbon disulphide in a small clean and dry flask, pour the solution into droppingfunnel *3*, and add it to the reaction flask dropwise. Periodically shake the flask. Let the solution stand for an hour. Distil off the carbon disulphide in a water bath at a temperature not exceeding 50 °C.

Cool the small amount of the phosphorus iodide solution remaining in the flask with ice. Separate the precipitated crystals using a filter No. 2 in a stream of an inert gas (see Fig. 64*b*) and wash them with dry carbon tetrachloride. Put the crystals into a weighed weighing bottle. Calculate the yield in per cent.

9. Preparation of Phosphorus Thiochloride. Put 33 ml of phosphorus trichloride and 12 g of finely triturated sulphur into flask *1* (Fig. 103). Place 3 g of anhydrous aluminium chloride into test tube *3*.

Heat flask *1* on a water bath. When the phosphorus trichloride boils, turn test tube *3* in its ground-glass joint and introduce the aluminium chloride in small portions into the reaction mixture. Stop the heating because the reaction is very violent. Have at hand a bath with cold water to be able to retard the reaction by cooling the reaction mixture if required. The reaction ends when the liquid in the flask stops boiling.

Pour the reaction mixture into the flask of an apparatus for fractional distillation under atmospheric pressure (see Fig. 20). Collect the fraction boiling at 125 °C. Pour the phosphorus thiochloride into a weighed drawn out test tube. Seal the ampoule (*wear eye protection!*). Weigh the ampoule and the remaining parts of the test tube. Write the equation of the reaction. Calculate the yield in per cent. Test the reaction of phosphorus thiochloride with water. Write the equation of the reaction. What is the oxidation state of sulphur in this compound?

15 CARBON

Indicate the position of carbon in Mendeleev's periodic table of the elements, the electron configuration and size of its atom, and its oxidation states.

15.1 COMPOUNDS

CARBON(IV) OXIDE

Preparation and Properties. Charge a Kipp gas generator for producing carbon dioxide, i.e. carbon(IV) oxide. Fill three dry jars with the gas (how can you convince yourself that the jars are

filled?). Light a small flame of a burner and pour out the contents of one of the jars onto it. What do you observe?

Using pincers or a tong, rapidly introduce a ribbon of burning magnesium into the second jar. What occurs? Write the equation of the reaction.

Introduce a spoon with red phosphorus ignited in the air into the third jar (*carefully, in a fume cupboard!*). Explain the observed phenomena.

Pass a stream of carbon dioxide into distilled water during 3-5 min. Test the solution with indicators. What processes occur when carbon(IV) oxide reacts with water? What ions are present in the solution? Write the equations of the reactions. Find the dissociation constants of carbonic acid (see Table 9).

SALTS OF CARBONIC ACID

1. Pour 2-3 ml of a 1 *N* sodium hydroxide solution into a test tube and pass carbon(IV) oxide through it until the solution becomes almost neutral. Heat the solution. What gas evolves? After this, test the reaction of the solution with indicators. Write the equations of the reactions and explain the difference in the action of the solutions on indicators. What salt hydrolyzes more—sodium carbonate or bicarbonate? Why?

2. See how the carbonates of various metals change when heated. For this purpose, roast the following salts in test tubes: basic copper carbonate, magnesium, calcium, and sodium carbonates, and sodium bicarbonate. Pass the evolving gas into lime water. Write the equations of the reactions. Explain why the thermal stability of the studied carbonates differs.

CARBON(II) OXIDE

Carbon(II) oxide is a strong poison! Perform the experiments only in a fume cupboard, lower the glass window!

Carbon(II) oxide (carbon monoxide) is prepared under laboratory conditions from formic or oxalic acid (prepare it only in one of these ways).

Preparation of Carbon(II) Oxide from Formic Acid and Studying Its Properties. 1. Assemble an apparatus as shown in Fig. 104. Pour 20 ml of a concentrated sulphuric acid solution into the 100-ml Wurtz flask, 15 ml of formic acid into the dropping funnel, a small amount of vaseline oil (a bubble counter) into the first wash bottle, and leave the second wash bottle empty. Put about 0.1 g of copper(II) oxide in the middle of a tube made from refractory glass, preferably with a widened part at its middle. Pour water into the crystallizer.

Carefully heat the flask with the sulphuric acid up to 60 °C and add the formic acid dropwise to it. Collect the evolving gas over the water in a small jar and test it with a burning splinter. What do you observe?

2. Having completely displaced the air from the apparatus (how can this be proved?), heat the part of the tube where the copper oxide is with the flame of a burner in a stream of carbon(II) oxide. How

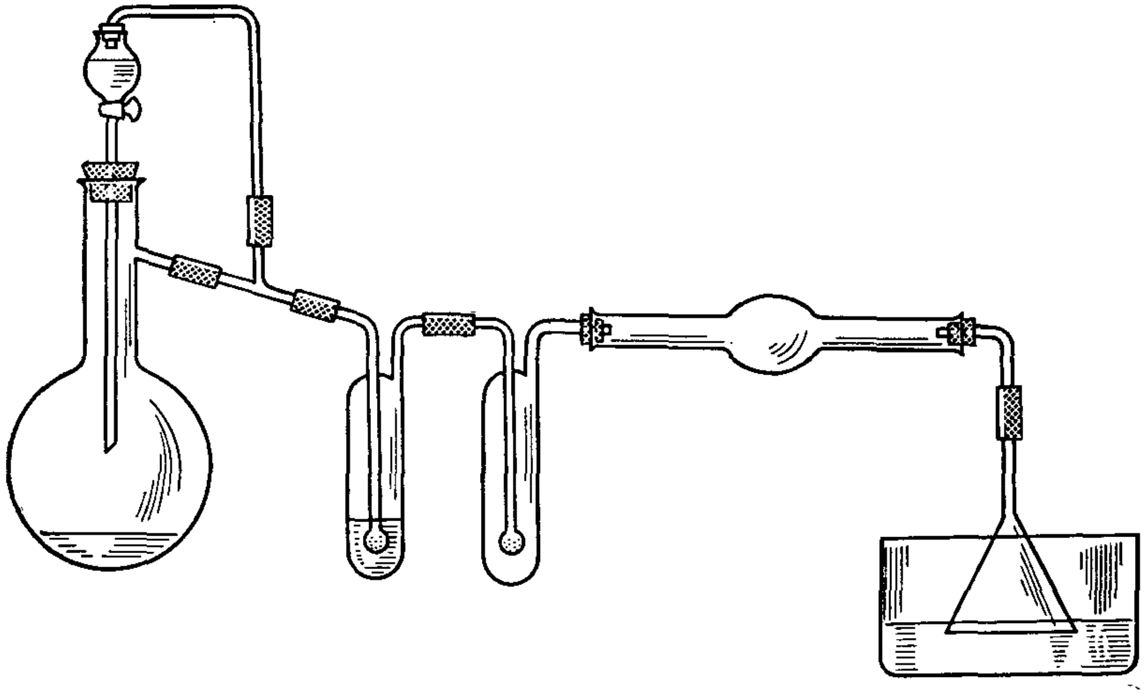


Fig. 104. Apparatus for preparing carbon(II) oxide and studying its properties

does the colour change? See how the evolving gas reacts with lime water. What properties of carbon(II) oxide are indicated by this experiment?

3. Remove the bath with water, remove the rubber tube with a bent glass tip from the end of the apparatus, and pass the carbon(II) oxide through ammonia solutions of silver nitrate and copper(I) chloride* poured into test tubes. What happens? Does the carbon(II) oxide exhibit the same properties in these reactions? How can one prove that carbon(II) oxide will evolve when the formed complex compound of copper(I) is heated?

After completing the experiments, cool the apparatus in a stream of carbon(II) oxide. Disconnect the refractory tube, extract the preparation from it and hand it in to your instructor.

Preparation of Carbon(II) Oxide from Oxalic Acid and Studying Its Properties. Assemble an apparatus as shown in Fig. 104, sub-

* Prepare an ammonia solution of a silver salt by adding an ammonia solution to a silver nitrate one until the silver oxide precipitate vanishes. Prepare an ammonia solution of copper(I) chloride by dissolving the latter in a concentrated ammonia solution.

stituting an open funnel with a long tube almost reaching the bottom of the Wurtz flask (see Fig. 53*a*) for the dropping funnel with an off-take tube.

Put 15 g of oxalic acid and 20 ml of concentrated sulphuric acid into the Wurtz flask. Pour a 10% sodium hydroxide solution into the first wash bottle instead of the vaseline oil (for what purpose?) and concentrated sulphuric acid into the second one. Put about 0.2 g of copper(II) oxide into the middle part of the refractory glass tube. Heat the reaction mixture in the Wurtz flask in a sand bath up to the beginning of vigorous evolution of the gas, after which remove the bath (*in the presence of your instructor!*).

Study the properties of the carbon(II) oxide as indicated above.

CARBIDES

Examine specimens of calcium, manganese, silicon, and tungsten carbides. How do the carbides differ as regards the action of water and acids on them?

Properties of Calcium Carbide. (*Perform the experiment in a fume cupboard!*) Assemble an apparatus (see Fig. 76) and check its tightness. Put one or two small pieces of calcium carbide into the dry Wurtz flask and pour water into the dropping funnel. By adding the water dropwise to the calcium carbide, pass a stream of the gas formed through the apparatus (for what purpose?), then collect the gas in a test tube over water and test it with a burning splinter. What happens? Write the equation of the reaction.

Upon completion of the reaction, filter the solution through a paper filter and add a few drops of phenolphthalein to it. What is observed?

Why can calcium carbide be called an acetylide, while beryllium and aluminium carbides cannot be given this name?

SUPPLEMENTARY EXPERIMENTS AND SYNTHESES

1. Preparation of Activated Carbon. Pour about 50 ml of water and put 35 g of charcoal into a 100-ml beaker and heat the latter until the charcoal sinks completely into the water. Extract the charcoal from the beaker, dry its surface with filter paper, and weigh it. Calculate the amount of water (in per cent) adsorbed by the charcoal.

For complete drying of the charcoal, put it into an iron crucible, cover it with a lid, and roast it during 20-30 min at 500 °C. Cool it in a desiccator. What is the essence of the carbon activation process?

2. Comparison of Adsorptivity of Activated and Non-Activated Carbon. Assemble an apparatus for preparing dry chlorine (see

Fig. 53*a*). Take two small U-tubes, close their upper openings with rubber stoppers, and their side offtakes with short rubber tubes having glass rods inserted into them. Weigh the tubes. Fill one U-tube with the prepared activated carbon, and the other with ordinary charcoal. Again weigh both tubes and connect them by a tee-piece to a source of chlorine.

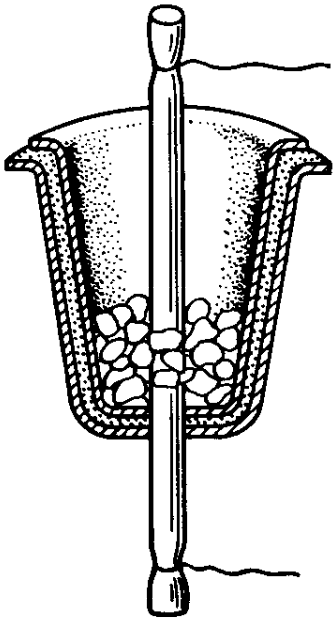


Fig. 105. Arrangement for preparing calcium carbide

Pass a stream of dry chlorine during 10-15 min through both tubes. What do you observe? Is heat liberated in this process?

Disconnect the U-tubes from the apparatus, close their side openings, let them cool, and weigh them. Use the obtained data to calculate the adsorptivity of carbon. Enter the data in a table.

Define adsorption. How is the sorptivity of sorbents expressed? How can the high adsorptivity of carbon be explained?

3. Preparation of "Dry" Ice. Put a bag made from a dense fabric onto the valve of a cylinder with liquid carbon dioxide and discharge a strong stream of the gas. What is observed? Measure the temperature of the solid carbon dioxide—"dry" ice. Put a small piece of the ice into a beaker and carefully add 3-5 ml of ethyl ether or ethanol (*extinguish all burners!*). Again measure the temperature. Write down the result.

4. Preparation of Calcium Carbide in an Electric Arc Furnace. Assemble an arrangement as shown in Fig. 105, using for this purpose two clay flower pots or chamotte crucibles of a different size with a hole in their bottom. Fill the space between the pot walls with dry sand. Insert a carbon electrode through the bottom holes of the pots and fasten it in a clamp. Triturate several pieces of carbon for arc lamps in a mortar. Prepare a similar powder from a natural chalk, better from calcium oxide. Weigh 8 g of calcium oxide and the calculated amount of carbon and thoroughly mix them. Spill the mixture into the inner pot of the arrangement* and lower a second upper carbon electrode so that it almost contacts the first one. Connect a rheostat for 40 V. Switch on the current, which should be 10-15 A. Carefully move the electrodes apart, trying to obtain the maximum

* The mixture can be made into beads. To do this, add to it thick starch size or a solution of dextrin in cold water until a thick dough is formed. Make beads 5 mm in diameter from it. Put the beads on a chamotte plate and dry them in a drying cabinet at a temperature of 100 °C.

size of the electric arc. The duration of the experiment depends on the amount of mixture taken. In the given case, 10-15 min are sufficient. See how the substance obtained reacts with water. Write the equations of the reactions.

5. Preparation of Calcium Carbide by Reacting Metallic Calcium with Carbon. Prepare a mixture from 5 g of calcium (crumbles) and 3 g of powdered coal. Put the mixture in a crucible, close it with

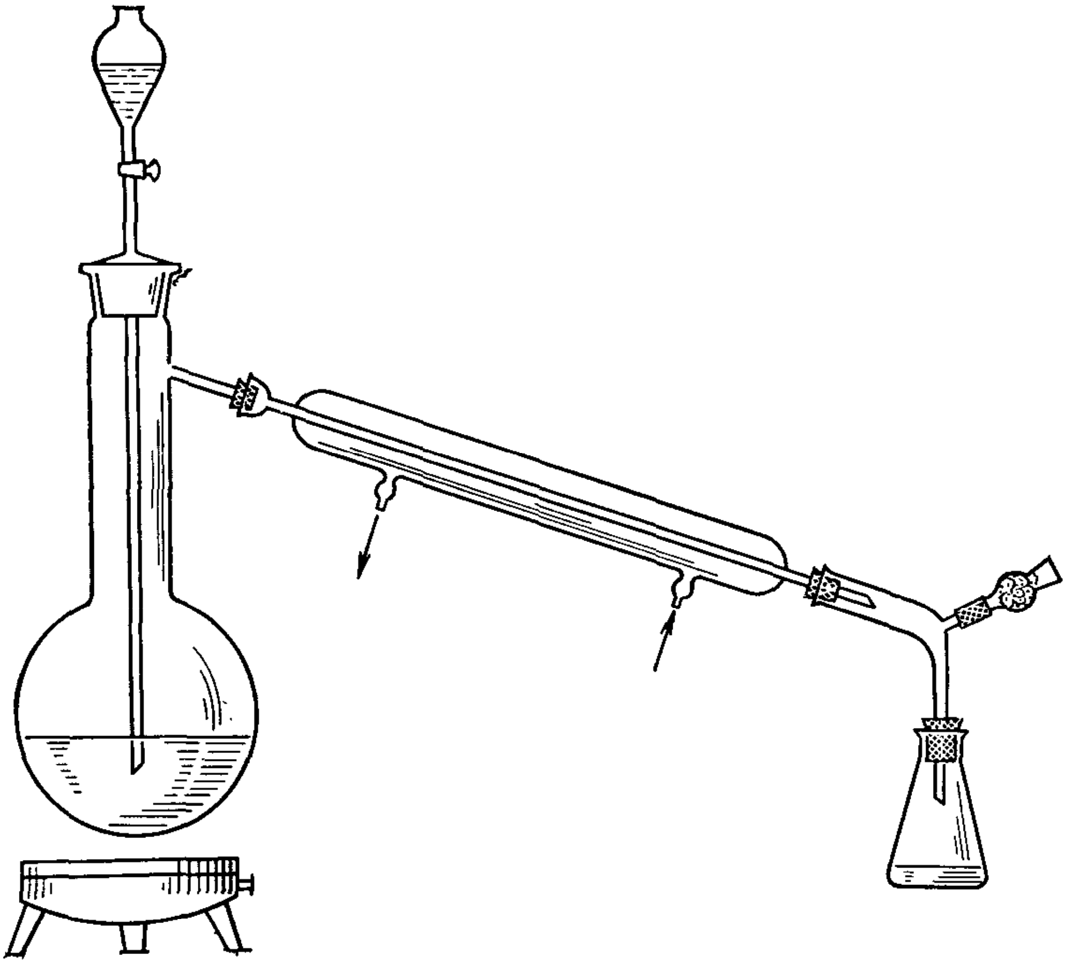


Fig. 106. Apparatus for preparing chloroform

a lid, and heat it up to a dark red glow (500-550 °C) during 5-10 min. After cooling, extract the sintered substance. See how it reacts with water. Write the equation of the reaction.

6. Preparation of Chloroform. First prepare chlorinated lime. To do this, add 60-80 ml of water to 60 g of pure slaked lime placed in a beaker. Thoroughly stir the mixture. Put the beaker into a bath with ice and pass chlorine purified from hydrogen chloride into the mixture during two hours.

Transfer the obtained chlorinated lime into the reaction flask of an apparatus for preparing chloroform (Fig. 106) and pour in 150 ml of water. Put a mixture of 20 ml of acetone and 20 ml of water into

the dropping funnel. The end of the latter must be below the level of the liquid in the flask. Pour 20 ml of water into the receiver flask to prevent evaporation of the distilled chloroform.

Add the acetone dropwise to the flask from the dropping funnel. Carefully heat the flask on an enclosed electric stove. If the reaction proceeds too violently, the reaction mixture may be thrown from the flask into the receiver. In this case, stop heating and cool the flask in a bath with cold water. Add the following portions of acetone as the formed chloroform is distilled off.

Separate the chloroform from the water with the aid of a separatory funnel. To purify the chloroform, place it into a separatory funnel and pour in a 2% sodium hydroxide solution. Mix the liquid well by shaking it. Separate the chloroform layer. Repeat the operation, replacing the sodium hydroxide solution with water. Dry the chloroform over anhydrous copper sulphate.

Transfer the dry chloroform into the flask of an apparatus for distillation under atmospheric pressure (see Fig. 20). Collect the fraction boiling at 62 °C. Weigh the substance and calculate its yield in per cent. Write the equation of the reaction of chlorinated lime with acetone.

16 THE COLLOIDAL STATE OF SUBSTANCES

16.1 PREPARATION OF COLLOIDAL SOLUTIONS

CONDENSATION

Preparation of a Sulphur Sol. Prepare a saturated solution of sulphur in ethanol in a test tube. Take 2-3 g of sulphur and 10 ml of ethanol for this purpose. The solution will become saturated after vigorous shaking during 15 min. Filter off the undissolved sulphur, measure off 5 ml of the solution, and carefully pour it dropwise into 20 ml of distilled water. Pour part of the colloidal solution into two test tubes in equal portions. Add 1 ml of water to the first tube and 1 ml of a barium chloride solution to the second one, and heat both tubes. What happens? How does the electrolyte affect the stability of the solution? Define a gel and a sol.

Preparation of an Iron(III) Hydroxide Sol. Heat 85 ml of distilled water in a conical flask up to boiling. Without removing the flask from the gauze, remove the burner and add 15 ml of a 0.1 *N* iron(III) chloride solution dropwise to the flask. Again boil the solution for several minutes. What occurs? How can the change in the colour of the solution be explained? Cool the solution and keep it for subsequent experiments.

Preparation of Manganese(IV) Oxide Sol. Add a 2% hydrogen peroxide solution to 5 ml of a potassium permanganate solution containing 14 g of salt per litre of solution until the violet colour disappears. Write the equation of the reaction. To determine the end of the reaction, proceed as follows: add a few drops of a saturated sodium chloride solution to a small sample and heat it. If a violet colour is noticeable, add more hydrogen peroxide solution to the main solution.

Subject the solution obtained to dialysis and treat the washing water first with phenolphthalein and then with methyl orange. Pour the solution into a number of test tubes and add to them 1 *N* solutions of salts of mono-, di-, and trivalent cations, respectively. What is observed? Explain the occurring processes.

DISPERSION

Preparation of a Silver Hydrosol by Electrolytic Dispersion. Assemble a device as shown in Fig. 107. Attach (better solder) insulated copper wires to the silver electrodes. Tightly fit sleeves (glass tubes) onto the electrodes so that only short ends of the latter protrude. Connect a rheostat for 18-20 Ω and 15 A. Pour distilled water into a small crystallizer. Immerse the end of one silver electrode into the distilled water up to a depth of 2 cm and secure it in such a position in a clamp of a stand. Set the rheostat to its maximum resistance. Switch on the current from the mains. Bring the second silver electrode, holding its sleeve in your hand, into contact with the first one for an instant and then rapidly move it 1-2 mm away. If no arc appears, reduce the resistance somewhat. By gradually decreasing the resistance, keep the arc continuous. In 5-10 min, switch off the current and filter the solution. See how the prepared colloidal solution of silver is affected by heating and the action of electrolytes.

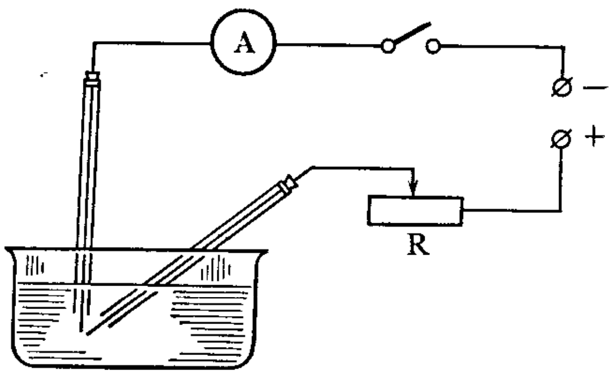


Fig. 107. Device for preparing a silver hydrosol by electrolytic dispersion

Preparation of an Aluminium Hydroxide Sol by Peptization. Prepare 100 g of a 10% aluminium chloride solution. Add an ammonia solution to it up to complete precipitation of aluminium hydroxide. Write the equation of the reaction. Wash the precipitate two or three times with water by decantation, and then on a filter in a Büchner funnel. When the precipitate becomes viscid, transfer it into a large beaker and add 50 ml of distilled water. Boil the contents

of the beaker and add a few drops of a 0.1 N hydrochloric acid solution. Continue the boiling for 1.5-2 hours, adding the acid dropwise from time to time. Calculate whether the amount of acid used is sufficient for transforming the hydroxide into aluminium chloride. See how the solution reacts with electrolyte solutions.

Which colloids are called lyophilic and which lyophobic?

16.2 PROPERTIES OF COLLOIDS

TYNDALL EFFECT

To detect the Tyndall effect, use a device (Fig. 108) consisting of a box divided into two equal parts by partition *1* with small aperture *2* at its middle. An electric lamp (100-150 W) is installed in outer wall *3* of the box. The second half of the box is provided with shelf *4* on which a beaker with a solution is placed. Observations are performed through an opening in the box door.

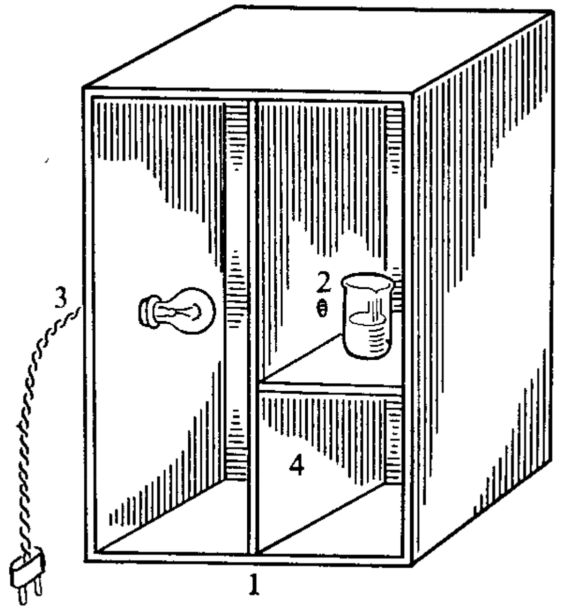


Fig. 108. Device for observing the Tyndall effect

Put a chemical beaker with a water-ethanol solution of sulphur onto shelf *4*. Switch on the lamp. Shut the door of the box and through an opening in it observe the luminous cone in the colloidal solution. Replace the colloidal sulphur solution with a true solution of sodium chloride in water. Is a luminous cone seen? Explain what causes a cone to appear when a light beam passes through colloidal solutions.

ADSORPTION OF COLOURED SUBSTANCES

Pour 50 ml of an aluminium chloride solution into a 100-ml beaker and precipitate aluminium hydroxide by adding an ammonia solution with stirring. How can the completeness of precipitation be determined? Filter off the aluminium hydroxide on a funnel with a filtering bottom and without removing the hydroxide from the filter, pass a solution of methylene blue through it. How can the vanishing of the colour of the solution be explained?

DIALYSIS

Prepare a collodion bag. To do this, thoroughly wash a test tube (up to complete wettability) and dry it in a drying cabinet. Fill the tube with collodion and rapidly pour it out again. Slowly rotate the test tube and let the collodion become uniformly distributed over its walls. Keep the tube inverted. Dry the film in the air up to the complete disappearance of an ether odour. Next rinse the test tube several times with distilled water to remove the unevaporated ether.

To extract the collodion bag from the tube, slightly separate the film from the edge of the tube and pour distilled water between the walls of the tube and the film. When the entire bag pulls away from the glass, pour several millilitres of water into it and carefully extract it from the tube.

Prepare a fused glass tube 2-3 cm long and about 1 cm in diameter. Carefully introduce the end of the tube into the upper part of the bag and fasten the bag to the tube with thread. Store the bag in a beaker in water.

Perform the dialysis of an iron(III) hydroxide solution prepared from iron(III) chloride. For this purpose, without extracting the bag from the water, insert a funnel into it and carefully fill it with an iron hydroxide sol. In 10 minutes, pour the water out of the beaker with a siphon and fill it with a new portion of water. Repeat the operation until chloride ions are no longer detected in the solution.

COAGULATION OF AN IRON(III) HYDROXIDE SOL

Pour 2 ml of the prepared colloidal iron hydroxide solution into each of several test tubes and add 2 ml of one of the following solutions of the same normality (0.1 *N*) to each of them: sodium chloride, barium chloride, aluminium chloride, sodium sulphate, aluminium sulphate, or monosubstituted sodium orthophosphate. What do you observe? How does the coagulating effect of an electrolyte depend on the sign and magnitude of the charge of its ions?

17 SILICON

Indicate the position of silicon in Mendeleev's periodic table of the elements, the electron configuration and size of its atom, and its oxidation states.

17.1 PREPARATION AND PROPERTIES

Preparation of Amorphous Silicon. (*Perform the experiment in a fume cupboard!*) Mix 1 g of dry quartz sand finely comminuted in an iron mortar with 1.5 g of powdered magnesium. Spill the mixture into a test tube fastened in a clamp of a stand over a sheet of iron or asbestos. First heat the tube over its entire length, and then strongly heat its bottom. What do you observe?

Break the test tube and transfer the product of roasting in small portions into a beaker containing 20 ml of a 25% hydrochloric acid solution. What gas evolves? How can you explain the observed flashes of light? Write the equations of the reactions. Filter off the silicon gathered on the bottom of the beaker.

Properties of Silicon. Treat a small amount of the prepared silicon in a test tube with a 20% sodium hydroxide solution. What happens? Write the equation of the reaction. See how silicon reacts with acids. Keep the remaining preparation for following experiments.

17.2 COMPOUNDS

SILICATES

Hydrolysis of Sodium Silicate. Dissolve several sodium silicate crystals in hot water and filter the solution if required. Test the action of the solution on phenolphthalein. Explain the change in the colour of the indicator.

Pour the solution into three test tubes. Pour dilute hydrochloric acid into the first tube. What happens? Write the equation of sodium silicate hydrolysis. Add a little dry ammonium chloride to the second tube. Stir the contents of the tube very well. What is the composition of the precipitate? Write the equation of the reaction. Pass a stream of carbon dioxide through the solution in the third tube. What do you observe? Write the equation of the reaction.

Preparation of Insoluble Silicates. Add solutions of calcium, iron(II), and cobalt salts to each of solutions of sodium silicate in separate test tubes. What occurs? Write the equations of the reactions.

You can obtain an "inorganic garden". For this purpose, pour 30-50 ml of a "liquid" glass solution into a beaker and drop crystals of cobalt, iron(II), aluminium, nickel, copper, and calcium salts into the solution. What is observed?

Hydrolysis of Glass. Heat a part of a glass tube until it softens and rapidly lower its end into a beaker with water. Repeat the operation several times. Pour off the water, transfer the fine glass fragments into a porcelain mortar, and grind them into a powder. Pour

in two or three drops of a phenolphthalein solution. Explain why a colour appears.

How is glass manufactured in the industry? What grades of glass do you know? What is the state of aggregation of glass? What is the composition of commercial soluble glass?

SILICIC ACIDS

Hydrogel of Silicic Acid. Pour 5 ml of a concentrated solution of soluble glass into a test tube, rapidly pour 3 ml of a 24% hydrochloric acid solution into it, and stir with a glass rod. What is observed? Write the equation of the reaction. How can you explain the formation of a gel?

Hydrosol of Silicic Acid. Add 1 ml of soluble glass to 6 ml of a 37% hydrochloric acid solution. Why does no gel form in this case? Does the acid solution obtained pass through a filter? Heat the solution almost to boiling, and then cool it. What happens? How can the silicic acid sol be separated from electrolytes in a solution?

FLUOSILICIC ACID

Preparation. Assemble an apparatus as shown in Fig. 109. Mix 2 g of dry quartz sand with 2 g of calcium fluoride. Transfer the mixture into a Wurtz flask and add 15 ml of a 96% sulphuric acid solution. Close the flask with a stopper. The funnel must touch the surface of the water in the beaker. Heat the flask. What do you observe? What gas evolves under the funnel? What substance precipitates? What is in the solution? Write the equations of the reactions. Keep the solution.

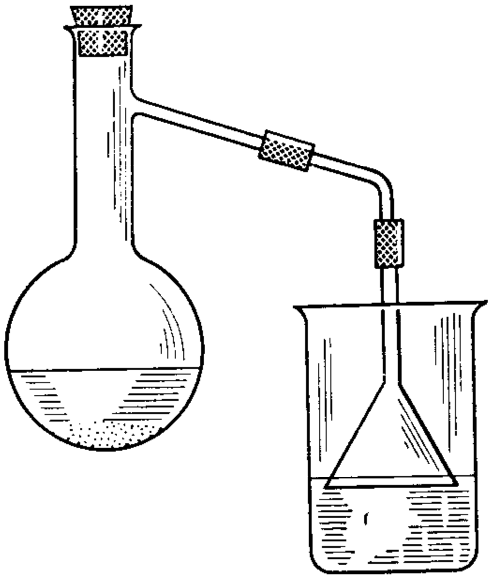


Fig. 109. Apparatus for preparing fluosilicic acid

Properties. See how a fluosilicic acid solution acts on various indicators. Study the reaction of this solution with metals, namely, zinc and magnesium.

SUPPLEMENTARY EXPERIMENTS AND SYNTHESES

1. Preparation of Crystalline Silicon. Pure crystalline silicon is prepared in a quartz ampoule (Fig. 110). Put 2.5 g of amorphous silicon and 0.5 g of iodine preliminarily purified by sublimation

into the ampoule (see p. 103). Connect the ampoule to a vacuum system and evacuate it during 20-30 min to a vacuum of 10^{-3} mmHg. Seal the ampoule in the vacuum (*wear eye protection!*).

Place the sealed ampoule into a two-zone furnace in which a temperature gradient of 1150-950 °C is maintained and leave it there for

Fig. 110. Quartz ampoule for preparing crystalline silicon

eight hours. Heat and cool the furnace gradually, retaining a constant difference of 200 °C between the temperatures of the zones.

Open the ampoule and purify the formed crystalline silicon from iodine by subliming the latter in vacuum. Explain the occurring processes.

2. **Preparation of Silicic Acid Anhydride.** Dissolve a small amount of potassium silicate in a minimum amount of water, filter the solution if necessary, and add a 37% hydrochloric acid solution up to a strongly acidic reaction. Transfer the solution into a porcelain bowl and evaporate it until dry in a sand bath. Wash the dry residue with warm water until the chloride ions are removed, then roast it and see how it reacts with solutions of an alkali and hydrofluoric acid (*in a lead bowl in a fume cupboard!*). Write the equations of the reactions. What is obtained when silicic acid anhydride is melted with alkalies?

3. **Preparation of Silicon Tetrachloride.** To prepare amorphous silicon, mix 2 g of dry quartz sand comminuted in an iron mortar with 3 g of powdered magnesium. Spill the mixture into a refractory test tube, secure it at an angle in a stand, and carefully heat first the entire tube, and then its bottom end more intensively until the mixture ignites. When the reaction ends, break the test tube, extract the product, crush it, and wash it (*in a fume cupboard, wear eye protection!*) with dilute hydrochloric acid until the flashes of light vanish. Filter off the silicon, wash it on the filter with distilled water, and dry it in the air.

The products of the reaction between silicon(IV) oxide and powdered magnesium can also be used to prepare silicon tetrachloride without the separation of free silicon.

Place the prepared silicon (or the product of reacting silicon(IV) oxide with magnesium) in a porcelain boat into quartz tube *1* of the apparatus shown in Fig. 111. Dry the apparatus and the silicon in a stream of dry carbon dioxide at 200 °C during one hour. Raise the temperature of the furnace to 400 °C and use a chlorine stream instead of that of carbon dioxide. Perform chlorination during 1.5-2 hours.

Collect the liquid silicon tetrachloride in a receiver flask provided with a calcium chloride tube or a wash bottle with a desiccator. Cool the receiver with a mixture of ice and table salt.

For complete purification from chlorine, distil the silicon tetrachloride over copper shavings in an apparatus for distillation under atmospheric pressure (see Fig. 20) and collect the fraction boiling at 57-59 °C. First thoroughly dry the distillation apparatus with

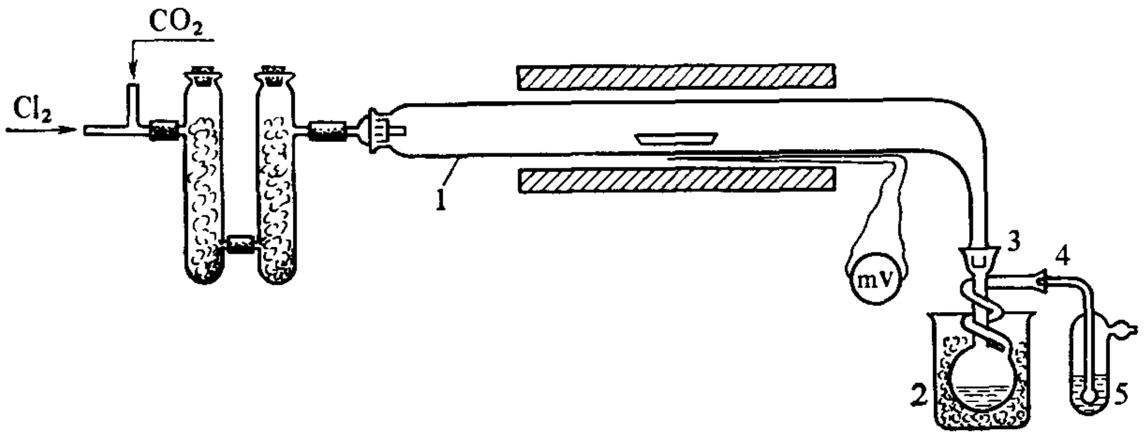


Fig. 111. Apparatus for preparing silicon tetrachloride and silicochloroform

a stream of dry carbon dioxide. Rapidly transfer the pure silicon tetrachloride into a weighed drawn out test tube in a dry chamber and seal it (*wear eye protection!*). Weigh the ampoule together with the remaining parts of the test tube. Write the equations of the reactions. Calculate the yield in per cent.

4. Preparation of Silicochloroform. Assemble an apparatus as shown in Fig. 111. Weigh 2-3 g of crystalline silicon, thoroughly wash it with a 10% hydrochloric acid solution, and dry it for one hour in vacuum (10^{-2} mmHg) at 60-70 °C. Put the boat with the silicon into tube *1*. Displace the air from the apparatus by passing an intensive stream of dry hydrogen chloride through it during 30-40 min. Without stopping the hydrogen chloride stream, switch on the furnace and slowly, during 30-40 min, raise the temperature of the reaction zone to 350-400 °C. Cool receiver *2* with a mixture of dry ice with acetone, maintaining the temperature of the cooling mixture at —70 °C. After hydrochlorination of the reaction mixture at 350-400 °C for two hours, stop the stream of hydrogen chloride.

Rapidly connect the receiver with the silicochloroform via standard ground-glass joint *3* to an apparatus for fractional distillation under atmospheric pressure (see Fig. 20) and close side arm *4* (see Fig. 111) with a glass stopper. Perform distillation and gather the fraction boiling at 34-37 °C.

18 BORON

Indicate the position of boron in Mendeleev's periodic table of the elements, the electron configuration and size of its atom, and its oxidation states.

18.1 PREPARATION AND PROPERTIES

(*Prepare boron in a fume cupboard, wear eye protection or a protective mask!*)

Preparation of Amorphous Boron from Boric Acid Anhydride. (Each student performs only one of the experiments for preparing amorphous boron.) Put 2 g of boric acid anhydride into an iron crucible or onto an iron plate and roast it (*if the boric acid anhydride contains moisture, then when it is heated with magnesium an explosion may occur!*). Triturate the boric acid anhydride as rapidly as possible (why?) in a mortar, weigh 1 g and mix it with 2 g of a magnesium powder. Place the mixture into a refractory test tube and fasten it in an inclined position in a clamp of a stand (*in a fume cupboard!*). First carefully heat the test tube with the mixture with the flame of a burner, and then strongly heat the bottom part of the tube. What do you observe?

When the reaction terminates, break the test tube cooled to room temperature in a mortar. Separate the substance from the glass and spill it in small portions into a beaker with 50 ml of a 10% hydrochloric acid solution (*in a fume cupboard!*). Which gaseous products form? Wash the hydrochloric acid off the boron with water and dry the boron in a drying cabinet. Write the equations of the reactions.

Preparation of Amorphous Boron from Borax. Weigh 15 g of borax. Transfer one-third of it into an iron crucible and heat it until all the moisture is removed. After the substance stops swelling, spill the remaining borax in small portions into the same crucible and again roast it. Cool the red-hot crucible in cold water, extract the glassy substance, and rapidly grind it into a powder. Prepare 8 g of a mixture of dehydrated borax and magnesium powder in a weight ratio of 2 : 1. After thorough stirring, put the mixture into a crucible and spill the powder of the fused borax on top of it. Close the crucible with its lid and roast it strongly on a gas burner. Write the equations of the reactions. Separate the boron in the same way as described in the preceding experiment.

Properties. Put a small amount of boron into a crucible. Put the latter into a hot crucible furnace. What happens? Write the equation of the reaction. How does boron react with acids and alkalies?

18.2 COMPOUNDS

BORIC ACID

Preparation from Borax. Dissolve 12 g of borax in 25 ml of water in a beaker with heating. What is the reaction of the solution to litmus and what is it due to? Write the molecular and net-ionic equations of the borax hydrolysis reaction. How can the hydrolysis of borax be facilitated? Calculate what amount of a 25% hydrochloric acid solution is needed to prepare boric acid from 12 g of borax. Measure off the calculated amount of acid, and taking a small excess amount, pour the acid into the hot borax solution. Let the solution cool slowly. What substance crystallizes? Filter off the crystals on a Büchner funnel, dry them between filter paper sheets, and recrystallize them from hot water, guiding yourself by the table of solubilities. Determine the product yield (in per cent). Keep the prepared boric acid for the following experiments.

Properties. 1. Prepare 2-3 ml of a saturated boric acid solution and test it with litmus and curcuma paper.

2. Evaporate the boric acid solution in a porcelain bowl until almost dry, add a little methanol, and light the evolving vapour. What is the flame colour due to?

3. Pour a drop of concentrated sulphuric acid and a drop of glycerin onto a watch glass and add a small amount of borax. Carefully stir the mixture with the eye of a platinum wire and introduce it into the flame of a burner. How is the flame coloured? Write the equation of the reaction.

BORIC ACID ANHYDRIDE

Preparation and Properties. Spill 5 g of pure boric acid into an iron crucible (better use a platinum crucible; why?). Cover the crucible with its lid and roast it in a muffle furnace at 800 °C up to complete removal of the water. What reactions occur? To extract the boric acid anhydride, immerse the bottom part of the red-hot crucible into cold water. Transfer the extracted substance into a bottle with a good stopper.

To test the viscosity of the boric acid anhydride, put a small amount of boric acid onto an iron plate, heat the latter, and when the substance begins to swell, pick up part of it with a glass rod and pull it. What is observed?

Treat a part of the boric acid anhydride in a test tube with water and determine the pH of the solution. Write the equations of the reactions.

COLOURED BORAX BEADS

Heat a small amount of borax in the eye of a platinum wire in the flame of a burner. After water stops evolving (how can this be established?), slightly cool the melt and wet it with a chromium(III) or cobalt(II) nitrate solution. Again heat the substance up to melting (in the flame of a burner). What colour does the substance acquire after cooling? Write the equation of the reaction. What does the colour of borax beads depend on?

SUPPLEMENTARY EXPERIMENTS AND SYNTHESES

1. Preparation of Boron Trichloride by Reacting Aluminium Trichloride with Boron Trifluoride. (*Perform the experiment in a fume cupboard!*) Assemble an apparatus as shown in Fig. 112.

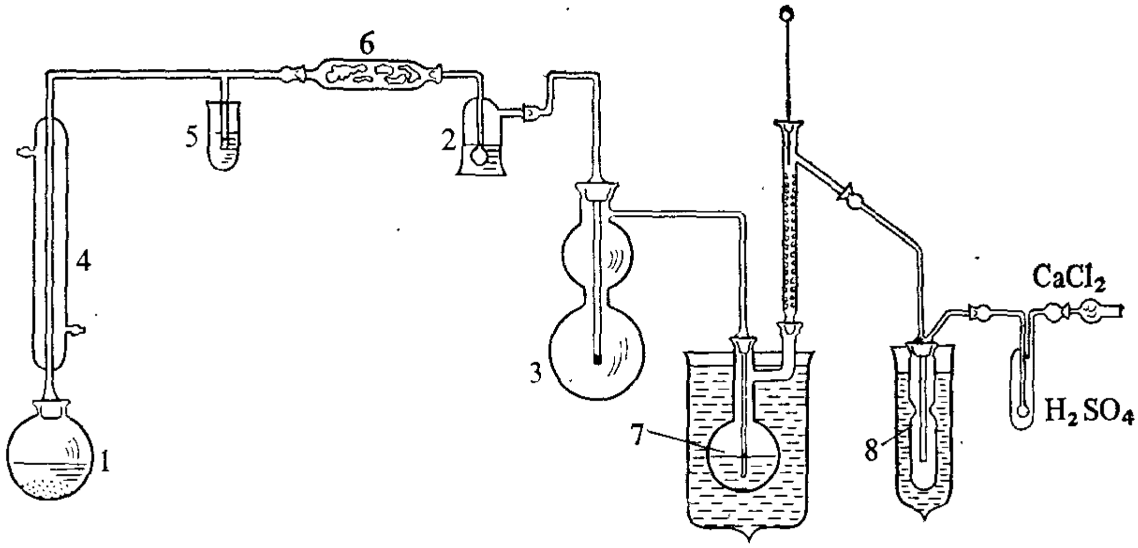


Fig. 112. Apparatus for preparing boron trichloride

Thoroughly dry all the parts of the apparatus. Put 80 g of sodium tetrafluoborate and 14 g of boric acid anhydride into 250-ml round-bottomed flask *1*; pour in a mixture of 60 ml of concentrated sulphuric acid and 20 ml of 20% oleum (d^{20} = 1.90). Pour concentrated sulphuric acid saturated with boric acid anhydride into wash bottle *2*, fill tube *6* with phosphoric anhydride applied onto glass wool, and pour glycerin into vessel *5* for functioning as a seal if the pressure in the apparatus rises. Spill 40 g of anhydrous aluminium trichloride into reaction vessel *3* through a funnel reaching the middle of the lower flask. Cool receiver *7* with a mixture of dry ice and ethanol and make sure that the receiver is completely submerged in the cooling mixture (see Fig. 112).

Heat flask *1* with the flame of a gas burner through an asbestos gauze and estimate the rate of gas evolution according to the number of bubbles in wash bottle *2*. When a uniform stream of gas is established, carefully (*wear eye protection!*) heat the bottom part of vessel *3* with the open flame of a burner. Do not let the products clog the gas-discharge tube. The amount of the aluminium chloride condensing in the upper part of the apparatus should be insignificant.

When 10-15 ml of boron trichloride gather in receiver *7* (in about one hour), disconnect vessel *3* and rapidly close the receiver with a stopper. Stop cooling the receiver and distil the boron trichloride

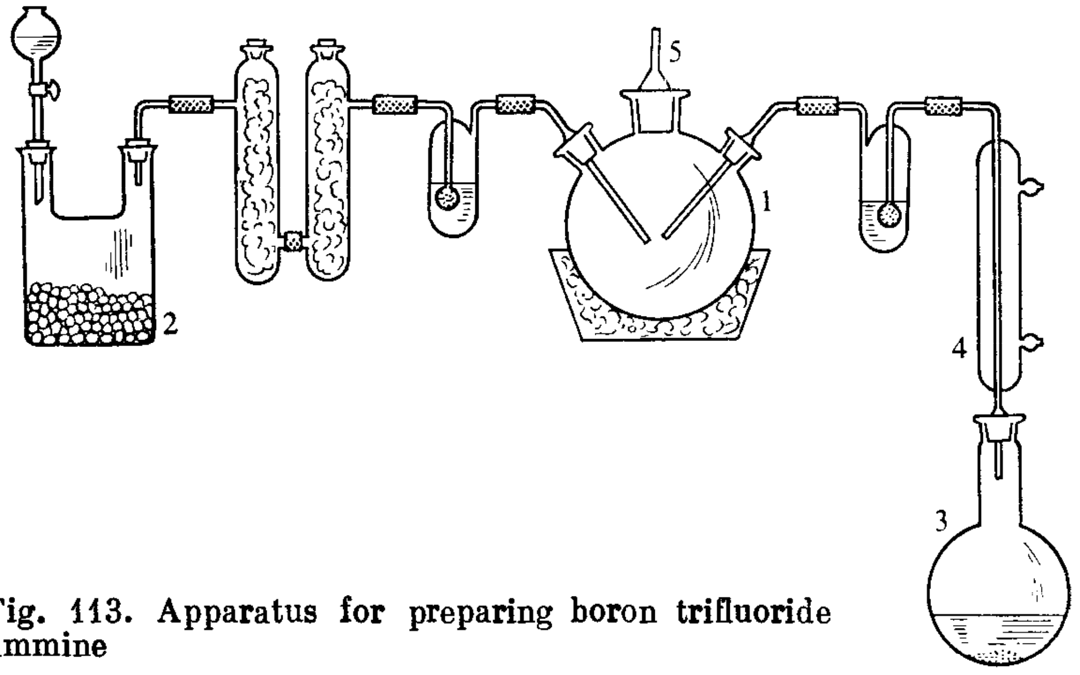


Fig. 113. Apparatus for preparing boron trifluoride ammine

into ampoule *8* cooled with a mixture of dry ice and acetone by heating flask *7* with your hand. When the ampoule is half filled, disconnect it and replace it with a new one. Close the half-filled ampoule with a stopper and immerse it into liquid nitrogen, and after some time rapidly seal it on a brazing burner (*wear eye protection!*).

2. **Preparation of Boron Tribromide.** (*Perform the experiment in a fume cupboard!*) Assemble a part of the apparatus shown in Fig. 112 beginning from vessel *3* without a gas-discharge tube. Put 54 g of aluminium tribromide and 13 g of potassium tetrafluoborate into reaction vessel *3* and close it. Carefully heat the vessel with the flame of a burner. Prepare and purify the boron tribromide in the same way as boron trichloride.

3. **Preparation of Boron Trifluoride Ammine.** Assemble an apparatus as shown in Fig. 113. Place flask *1* into a bath with ice. To produce ammonia, spill solid granulated sodium or potassium hydroxide into bottle *2*. Pour a concentrated ammonia solution into the dropping funnel.

To prepare boron trifluoride, mix 50 g of potassium fluoborate and 9 g of boric acid anhydride in flask *3*, and pour 25 ml of anhydrous sulphuric acid into the mixture. Prepare the anhydrous sulphuric acid by adding the relevant amount of 65% oleum to a 96% sulphuric acid solution (*carefully, wear eye protection!*).

Before the synthesis, displace air from the apparatus with a strong stream of ammonia. Next pass the ammonia and boron trifluoride through the apparatus at the same rate. (If excess boron trifluoride is introduced, it evolves in the form of white smoke from discharge opening *5*.)

Boron trifluoride ammine deposits on the walls of flask *1* in the form of a bulky, loose powder. To prevent clogging of the tubes feeding in the gases, they must be at least 7-8 mm in diameter. Gather half of the prepared substance in a drawn out test tube and seal it.

Test the reaction of boron trifluoride ammine with water. Dissolve boron trifluoride ammine in a minimum amount of water and evaporate it in a water bath until almost dry. Cool the solution. Examine the separated crystals under a microscope.

19 ALKALI METALS

Indicate the position of the alkali metals in Mendeleev's periodic table of the elements, the electron configurations and sizes of their atoms, and their oxidation states. Which of the alkali metals forms more stable diatomic molecules in their vapours? Which compounds of the alkali metals are encountered in nature? How are these metals prepared in a free state?

19.1 PROPERTIES

When working with metallic sodium and also with other alkali metals, beware of water! Extract these metals from kerosene only with pincers, never with your hands! Hand in trimmings of alkali metals and also unused metal to the laboratory assistant. Never throw trimmings of these metals into waste jars and sinks!

Reaction of Alkali Metals with Water. (*Work in a fume cupboard, wear eye protection or a protective mask!*) Fill a crystallizer with water and put it into a fume cupboard. Make a small box (2 × 2 cm) from filter paper and put a small piece of purified lithium the size of a pea into it. With the window of the fume cupboard half lowered, carefully place the box with the lithium into the crystallizer with water. Observe what occurs. Test the action of the formed solution

on phenolphthalein. Perform similar experiments with sodium and potassium. Write the equations of the reactions.

Compare the chemical activity of the studied alkali metals. What does it depend on? Why does lithium head the electrochemical series of the metals? Find the values of the standard electrode potentials of the alkali metals (see Appendix 1, Table 21).

Preparation of Sodium Amalgam. (One student prepares this experiment and demonstrates it to the class.) (*Perform the experiments in a fume cupboard with the window half lowered*; *carry out all experiments with mercury in trays with high walls!*)

a. Put a small amount of mercury into a dry porcelain mortar. Extract a small piece of metallic sodium from kerosene with pincers (*in the presence of your instructor!*), put it onto filter paper on dry glass in a fume cupboard, and dry it from the kerosene. Remove the oxide film from the sodium surface with the tip of a lance or penknife and cut off several small pieces. Put one of the sodium pieces into a mortar with dry mercury and carefully grind it with a pestle. What do you observe? Grind some more pieces of sodium in the same way until the amalgam thickens. Drop a small amount of the amalgam into a beaker with water. What happens? Write the equations of the reactions.

b. Transfer a part of the amalgam into a wide test tube or beaker and pour 3-5 ml of a saturated ammonium chloride solution onto it. Comment on your observations. What happens to the contents of the test tube after some time? Write the equations of the reactions.

19.2 COMPOUNDS

OXIDES

Preparation of Lithium, Sodium, and Potassium Oxides. (*Perform the experiment in a fume cupboard!*) Put a small piece of metallic sodium or potassium onto the lid of a crucible, heat the lid from below, and when the metal melts, ignite it from above with the flame of a burner (*lower the fume cupboard window!*). When all the metal has burned, cool the product and dissolve it in 2-3 ml of distilled water (*carefully, unburned alkali metal may remain!*). Add a potassium iodide solution acidified with a dilute sulphuric acid solution and two or three drops of a starch size to the prepared solution. What is observed? What substances form when sodium and potassium burn in the air? How can the oxides of these elements be prepared?

Run a similar experiment with metallic lithium. What forms in this case? How can lithium peroxide be prepared? What products form when rubidium and cesium react with the oxygen of the air?

Why do some of the alkali metals form oxides, while others form peroxides when they burn in the air? How does the stability of the alkali metal oxides and peroxides change (from lithium to cesium) when heated? Why is the formation of peroxides and also of ozonides the most characteristic of the alkali metals?

HYDROXIDES

How does the solubility of the alkali metal hydroxides change in the series from lithium to cesium? How are the alkali metal hydroxides produced in the industry?

Preparation of Sodium Hydroxide from Sodium Carbonate. Dissolve 14 g of anhydrous sodium carbonate in 100 ml of water. Pour the solution into a 250-300-ml round-bottomed flask. Put pieces of broken chamotte crucible on the bottom of the flask (for what purpose?). Fasten the flask in a stand so that a small space remains between the gauze and the bottom of the flask. Heat the solution in the flask up to boiling and add 8-10 g of triturated calcium hydroxide (in small portions). Insert a funnel into the neck of the flask (for what purpose?) and boil the solution during one hour, adding water from time to time to keep the volume constant. After cooling, filter the solution and measure its volume and density. Use the density value to determine the percentage of sodium hydroxide in the solution. Hand in the alkali solution to the laboratory assistant.

Find the solubilities of calcium carbonate and hydroxide from the relevant tables. Write the equations of the reactions. Explain the course of this process. Can this method be used to prepare a sodium hydroxide solution with a high concentration? Can a similar method be used to prepare potassium hydroxide?

SALTS

Preparation of Sodium Bicarbonate. Saturate 50 ml of a 10% ammonia solution with sodium chloride in the cold. Filter the solution, pour it into a flask, and close it partly with a cork stopper accommodating a gas-discharge tube almost reaching the bottom of the flask. Pass carbon dioxide (from a cylinder or a Kipp gas generator) into the solution until a precipitate stops separating (during 1-1.5 hours). Separate the crystals on a Büchner funnel, wash them with ethanol, and dry them at room temperature in the air. Write the equations of the reactions. What impurities does the product contain?

Using the relevant tables, find the solubilities of the salts that can form in an ammonia solution of sodium chloride saturated with carbon dioxide. Explain the sequence of the processes occurring in this reaction mixture. Recrystallize the product from warm water (about 50 °C).

Dissolve a small amount of the salt in distilled water and test the action of the solution on litmus, phenolphthalein, and a universal indicator. Explain what you observe.

Preparation of Sodium Carbonate. Put about 0.5 g of sodium bicarbonate onto the bottom of a porcelain crucible and roast it on a gas burner during 20-30 min.

Dissolve the roasted substance (what is its composition?) in water and test the reaction of the solution with phenolphthalein, methyl red, and a universal indicator. Comment on your observations.

What salt is hydrolyzed more: sodium carbonate or bicarbonate? Why?

Write the formulas of the substances called soda crystals (washing soda), calcined soda, baking soda, and caustic soda.

Lithium Carbonate. Add a saturated sodium carbonate solution to 2-3 ml of a saturated lithium sulphate or chloride solution. What do you observe? Write the equation of the reaction. Acquaint yourself with the solubility of the alkali metal carbonates in water.

Sparingly Soluble Sodium and Potassium Salts. 1. Add several drops of a zinc uranyl acetate solution to 0.5 ml of a neutral solution of a sodium salt. Note the colour of the precipitate. Write the equation of the reaction.

2. Pour a solution of sodium hydrotartrate or sodium perchlorate into 1 ml of a saturated neutral solution of a potassium salt. If a precipitate does not form immediately, accelerate its appearance by rubbing a glass rod against the internal walls of the test tube. Write the equation of the reaction.

What other sparingly soluble salts of sodium, potassium, and lithium do you know? What reactions are used in the industry to separate the alkali metals?

Colouring of a Flame by Lithium, Sodium, and Potassium Salts. Introduce a platinum or nichrome wire into the colourless flame of a burner. If the flame becomes coloured, wash the wire with pure hydrochloric acid and roast it in the burner flame until the latter becomes colourless. Wet a platinum wire in a potassium chloride solution and introduce it into the colourless flame of the burner. What do you observe? Perform similar experiments with solutions of sodium and lithium chlorides. Observe the colouring of the flame by the potassium salts through an indigo prism.

SUPPLEMENTARY EXPERIMENTS AND SYNTHESES

(Hand in all the obtained preparations to your instructor.)

1. Preparation of Metallic Cesium (Rubidium). Place quartz vessel *2* (Fig. 114) into an inclined furnace. Calculate the amount of

cesium (rubidium) carbonate that is needed to prepare 5 g of the alkali metal. Prepare a thoroughly triturated mixture of the calculated amount of the carbonate and a four-fold excess of powdered metallic zirconium. Put the reaction mixture into steel test tube *1* (what is a steel test tube needed for?) and place the latter into quartz vessels *2* (*in the presence of your instructor, wear eye protection!*).

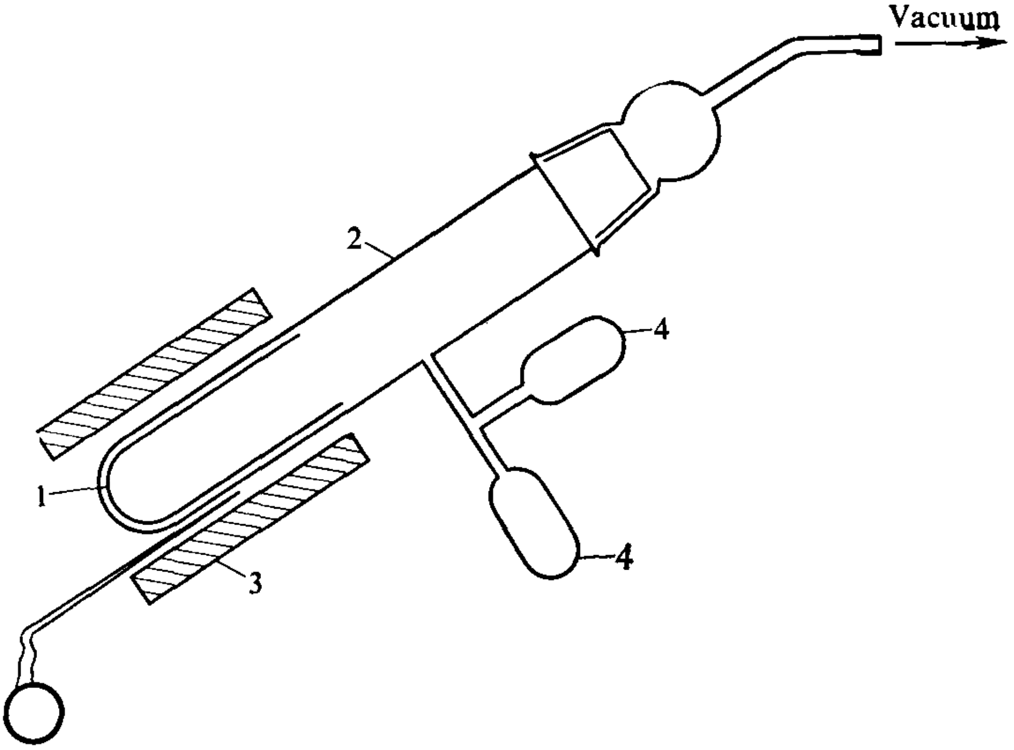


Fig. 114. Arrangement for preparing metallic cesium (rubidium)

Connect vessel *2* through a ground-glass joint to a vacuum system. When a vacuum of the order of 10^{-3} mmHg is reached in the system, switch on furnace *3*. Gradually raise the temperature in the furnace to 500 °C and keep the apparatus under these conditions until a constant vacuum sets in with a value of 10^{-3} mmHg. This indicates that the water vapour and gases have been removed from the system. Carefully, to prevent ejection of the reaction mixture, raise the temperature in the furnace to 650-700 °C. Continue the heating until condensation of the metal vapour in ampoule *4* stops.

To purify the cesium (rubidium) from the admixture of the zirconium used for reduction, repeat the distillation from one ampoule into another one. For this purpose, carefully heat the alkali metal in the ampoule with a gas burner until boiling begins and perform distillation slowly (during 0.5 hour). After this, seal the ampoule with the metal. Write the equation of the reaction.

2. Preparation of Lithium Hydride. (*Perform the experiment in the presence of your instructor!*) Assemble an apparatus as shown in

Fig. 115. To prepare hydrogen, use a large freshly charged Kipp gas generator with a sufficient amount of acid. The latter must remain in the upper sphere even when it rises in the middle one above the zinc charge. Check the intensity of hydrogen evolution. Pour an acidified potassium permanganate solution into wash bottle *1* and a 96% sulphuric acid solution into bottle *2*. Fill U-tube *3* with glass wool mixed with phosphoric anhydride, and insert an iron tube into porcelain tube *5*. Pour water into the crystallizer. Check the tightness of the entire apparatus.

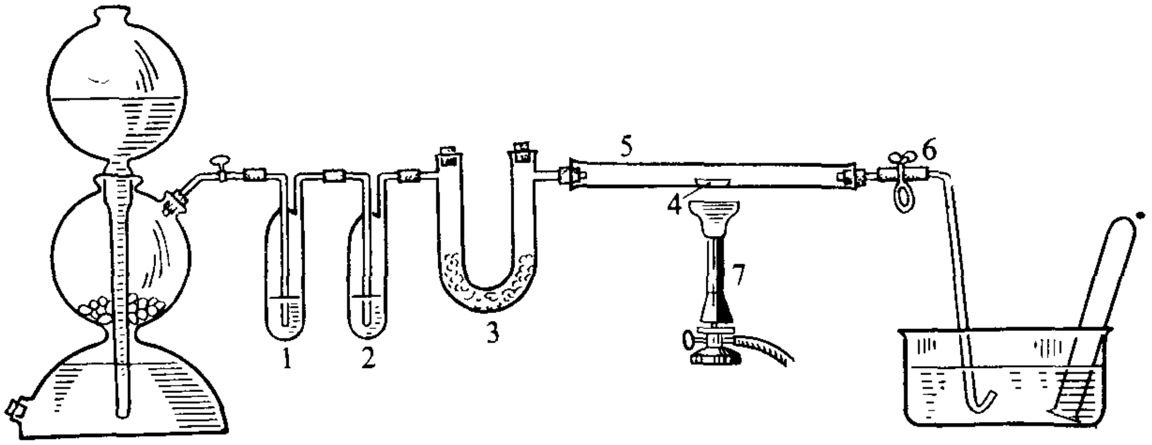


Fig. 115. Apparatus for preparing lithium hydride

Put 1 g of freshly cut metallic lithium cleaned of kerosene into iron boat *4* and place the latter into the middle part of the iron reaction tube. Again check the tightness of the apparatus and fill it with hydrogen. To do this, open clamp *6* and displace the air from the entire apparatus with a stream of hydrogen. Check the purity of the hydrogen evolving from the apparatus. Close the clamp and open the stopcock of the Kipp gas generator as far as it goes (not a single gas bubble should break through the washing liquids!). Put an asbestos sleeve onto tube *5* and begin to heat the tube where the boat with the metallic lithium is. Hold gas burner *7* with a flat "dovetail" nozzle in your hand while heating. At a temperature close to 500 °C, the lithium reacts with the hydrogen. Hydrogen bubbles begin to pass through wash bottles *1* and *2*. If the reaction proceeds violently, stop heating the reactor, and leave the apparatus under the pressure of the hydrogen.

When the absorption of the hydrogen stops (how can this be determined?), cool the apparatus to room temperature in a hydrogen atmosphere. Write the equation of the reaction. Extract the boat from the tube. What is the colour of the product? See how lithium hydride reacts with water. What is the nature of the bond in a lithium hydride molecule?

3. Preparation of Lithium Peroxide. *a. Preparation of Lithium Hydroxide Monohydrate.* Put 5 g of lithium sulphate into a 400-ml

beaker and add 20 ml of water to the salt. Thoroughly mix the components. Place the beaker with the solution in a water bath. After the solution becomes hot, gradually add (without stopping the heating) a barium hydroxide solution saturated at room temperature (baryta water) up to complete precipitation.

Separate the precipitate from the solution by filtration through a smooth filter (fine-texture filter paper—Whatman No. 2 or Schleicher and Schnell No. 489 Blue Ribbon). Transfer the filtrate into a Wurtz flask connected to a water-jet pump. Place the flask in a water bath and evaporate the solution in the vacuum produced by the pump up to a volume of about 20 ml.

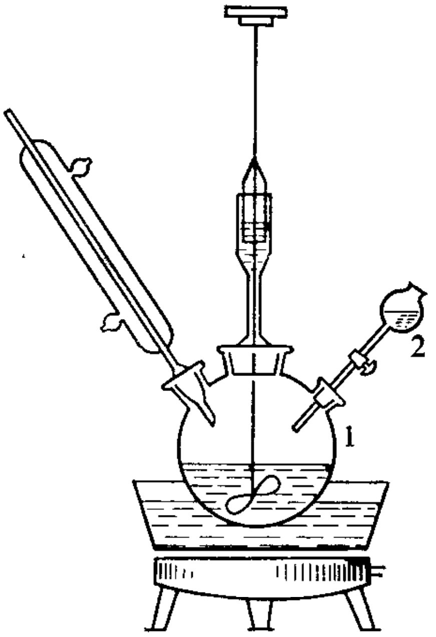


Fig. 116. Apparatus for preparing lithium peroxide

Rapidly transfer the solution into a bowl and cool it to room temperature. Filter off the precipitated crystals using a glass filter No. 3 (about 400 mesh).

b. Preparation of Lithium Peroxide Monohydrate. Assemble an apparatus as shown in Fig. 116. Transfer the prepared lithium hydroxide into flask *1* and pour 50 ml of ethanol into it. Switch on the mechanical mixer, and heat the flask in a water bath (*use an electric stove with an enclosed coil!*) until the reaction mixture boils. Without switching off the mixer, add 20 ml of a 30% hydrogen peroxide solution dropwise from funnel *2* and keep the flask in the water bath for another 1-1.5 hours.

Separate the formed precipitate of lithium peroxide monohydrate from the mother liquor by filtration and wash it twice on the filter with 5-ml portions of absolute ethanol. Dry the substance in the air.

c. Preparation of Anhydrous Lithium Peroxide. Place the prepared lithium peroxide into a test tube and connect it to a vacuum system via a ground-glass joint. After the vacuum reaches 10^{-1}-10^{-2} mmHg, carefully heat the tube to 80-120 °C. Keep the substance in the vacuum with heating during 30-40 minutes. Transfer the lithium peroxide into a previously weighed weighing bottle, weigh the substance, and calculate the yield in per cent.

Add distilled water to a small amount of the lithium peroxide. See how the mixture reacts with solutions of potassium permanganate and potassium iodide acidified with sulphuric acid (add two or three drops of a starch size to the potassium iodide solution). What do you observe? Write the equations of the reactions.

4. Preparation of Sodium Peroxide. Assemble the arrangement shown in Fig. 117. Pour a little vaseline oil into wash bottle *1* and leave bottle *2* empty. Put 2-3 g of cleaned metallic sodium into porcelain boat *3* and place it into quartz or refractory glass tube *4*. Cover the tube with asbestos and switch on the water-jet pump connected to the arrangement (*install protective bottles ahead of the pump!*). Heat the part of the tube where the boat with the sodium is with a gas burner flame. When the sodium ignites, reduce the heating. Suck

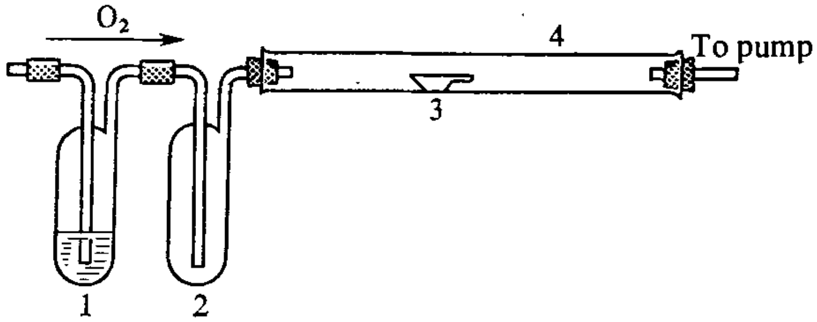


Fig. 117. Arrangement for preparing sodium peroxide

a strong stream of air through the arrangement until all the sodium reacts. When the reaction terminates, cool the arrangement in a stream of air. Extract the boat and spill the sodium peroxide into a weighing bottle.

Dissolve a small amount of the sodium peroxide in distilled water. See how this solution reacts with solutions of potassium permanganate and potassium iodide acidified with sulphuric acid (add two or three drops of a starch size to the potassium iodide solution). What is observed? Write the equations of the reactions.

5. Preparation of Lithium Iodide. Assemble an apparatus (see Fig. 116). Put 2 g of freshly sublimed dry iodine into three-neck flask *1*. Fill the cooler with cold water. Add 75 ml of absolute ether from the dropping funnel to the flask. Cool the latter in a bath with cold water. Extract the dropping funnel and carefully introduce lithium hydride through the side neck with stirring until the iodine colour vanishes (one or two hours). Replace the dropping funnel in the flask and continue to stir the reaction mixture until the evolution of hydrogen and the boiling of the ether stop. After this, add 50 ml more of the ether and boil the mixture for an hour in a water bath (*use an electric stove with an enclosed coil!*).

Rapidly pour over the solution into a round-bottomed flask and close it with dark paper (the solution turns yellow in the light). Connect the flask to a water-jet pump via an empty trap and drying columns with a granulated alkali (see Fig. 119*b*, p. 196).

Distil off the major part of the ether in the vacuum produced by the pump at room temperature, and then at 40 °C (in a water bath).

Transfer the white or slightly yellow salt into a weighed weighing bottle and weigh the product. Calculate the yield in per cent.

What will happen if the ether solution is cooled to —20 °C without evaporation in a vacuum?

6. **Preparation of Potassium Hydroxide by the Electrolysis of a Potassium Chloride Solution.** Assemble an electrolyzer (see Fig. 130, p. 231). Place small cylinder *2* (8 cm in height and 4 cm in diameter) made from uncalcined clay into 0.5-litre thick-walled beaker *1*. Pour a saturated potassium chloride solution into both vessels so that the level of the liquid in them will be the same. Add a few drops of phenolphthalein to the electrolyte. Use carbon rod *4* as the anode and thick iron wire *3* as the cathode. Secure both electrodes with corks in the electrolyzer lid. A d-c source at 10 V is needed for the experiment. After assembling the electrolyzer, switch on the current. What happens in the anode and cathode compartments? Write the equations of the reactions. What substances can form in the absence of a diaphragm?

After 40 or 50 minutes of electrolysis, switch off the current and determine the concentration of the obtained potassium hydroxide solution by titration.

7. **Preparation of Sodium Sulphate and Its Hydrates.** Calculate the amount of Glauber salt needed to saturate 20 ml of water at 32 °C. Prepare at this temperature a saturated sodium sulphate solution, filter it into two small flasks and into a dry test tube.

Anhydrous Sodium Sulphate. Heat the solution in the test tube until it boils. What do you observe? Separate the crystals from the mother liquor and examine their shape under a microscope.

Sodium Sulphate Decahydrate. Drop a crystal of Glauber salt into the sodium sulphate solution in one of the flasks. Examine the shape of the crystals precipitating from the solution at room temperature (below 25 °C) under a microscope.

Sodium Sulphate Heptahydrate. Heat the sodium sulphate solution in the second flask to 32 °C in a water bath. When the liquid becomes transparent and contains no crystals, close the mouth of the flask with cotton wool and carefully, without shaking the contents, put it into a cooling mixture (ice with a small amount of sodium chloride). In 10 or 15 minutes, carefully extract the flask with the sodium sulphate solution. Note the shape of the crystals separated in the given case.

Lower a small crystal of Glauber salt into the solution. Explain what happens. Draw curves of the solubility of anhydrous sodium sulphate and its crystallohydrates. Acquaint yourself with the phase diagram of the sodium sulphate-water system. In what parts of the diagram is the system invariant, monovariant, or divariant?

8. **Determining the Transition Temperature of Sodium Sulphate Decahydrate to the Anhydrous Salt.** Assemble an arrangement (see

Fig. 49). Fill inner test tube *1* containing a thermometer having 0.1 K graduations with a mixture prepared from crystalline sodium sulphate decahydrate and its solution saturated at room temperature. Outer test tube *6* plays the role of an air bath. Pour an amount of water into beaker *4* such that test tube *6* is immersed into it as deep as possible. Maintain the temperature of the water in the beaker at about 38-40 °C.

Extract inner test tube *1* with the crystals from outer tube *6* and immerse it directly into the water in the beaker. When part of the crystals melt and the reaction substance is a liquid, wipe tube *1* outside and return it into tube *6* immersed into the beaker with water. Begin to record the readings of the thermometer in test tube *1* every 30 seconds with constant stirring of the tube contents. Why does the temperature stop rising? Terminate this part of the experiment when the temperature of the reaction mixture rises to 34-35 °C. Draw a heating curve of the temperature against the time.

Heat test tube *1* with the reaction mixture to 35-40 °C, place it together with outer test tube *6* into a beaker with water whose temperature is 25-28 °C, and record the temperature every 30 s. If the temperature of the reaction mixture dropped continuously to below 30 °C, add a crystal of Glauber salt to the contents of the test tube and repeat the heating-cooling cycle until a temperature plateau is obtained. Plot the temperature against the time. What is the temperature plateau in cooling due to?

Using published data, draw a phase diagram of the sodium sulphate-water system. Proceeding from the phase rule, determine which parts of the diagram will characterize invariant, monovariant, and divariant systems. What is meant by the transition point?

9. Preparation of Potassium Nitrate. Pour 25 ml of water into a beaker and dissolve 12 g of sodium nitrate in it upon heating. Add an equivalent amount of potassium chloride to the solution. Cover the beaker with a watch glass and heat it on a gauze with a small burner flame until crystals precipitate. Can crystals form without evaporation of the solution? Rapidly pour the hot liquid into a porcelain bowl and let it stand until crystals form.

Table 4. SOLUBILITY OF SUBSTANCES IN GRAMMES PER 100 g OF WATER

Substance	Solubility at temperature		Substance	Solubility at temperature	
	10 °C	100 °C		10 °C	100 °C
Potassium nitrate	21	246	Potassium chloride	31	56
Sodium chloride	36	40	Sodium nitrate	81	174

Examine under a microscope the shape of the crystals remaining in the beaker and in the bowl. Filter off the crystals formed in the porcelain bowl, dry them in the air, and determine the yield in per cent. Using Table 4 containing the solubilities of the salts that can form in the solution, explain the conditions of precipitation of the salts formed from the solution.

20 BERYLLIUM, MAGNESIUM, CALCIUM, STRONTIUM, BARIUM

Indicate the position of beryllium, magnesium, calcium, strontium, and barium in Mendeleev's periodic table of the elements, the electron configurations and size of their atoms, and their oxidation states.

20.1 BERYLLIUM, MAGNESIUM, AND THEIR COMPOUNDS

(Beryllium compounds are poisonous. Wash your hands after working with them. Hand in all residues of beryllium compounds to the laboratory assistant!)

What position do beryllium and magnesium occupy in the electrochemical series of the metals?

Properties of Magnesium. 1. How does magnesium react with dilute and concentrated acids? Write the equations of the reactions of magnesium with nitric, sulphuric, and acetic acids.

2. Grip a small magnesium ribbon (1-2 cm long) with crucible tongs and burn it in the air over a porcelain bowl. Add a few drops of a concentrated alkali solution to the substance obtained and smell the evolving gas. With what components of the air does magnesium react?

3. Pour 2-3 ml of water and put a small piece of magnesium into each of two test tubes. Add a small amount (0.5-1 g) of ammonium chloride to one of the tubes. What occurs? Heat the solution up to boiling. Explain the processes that take place. Write the equations of the reactions. Why does magnesium react more actively with water in the presence of ammonium ions?

HYDROXIDES

Preparation and Properties of Beryllium Hydroxide. Add a 10% ammonia solution dropwise to 4-5 ml of a 3% beryllium sulphate solution up to the complete formation of a precipitate. See how beryllium hydroxide reacts with 10% solutions of sodium hydroxide (use a minimum amount of the alkali) and acids. Boil the alkaline

solution of beryllium hydroxide. What precipitates? Why does the precipitate fail to disappear when cooled?

How can you explain the fact that when an aqueous solution of an alkali metal beryllate is heated beryllium hydroxide precipitates, while when an aqueous solution of beryllium chloride or sulphate is heated no beryllium hydroxide precipitate forms?

Write the equations of the reactions and explain the occurring processes. What is the coordination number of beryllium in sodium beryllate? What type of orbital hybridization occurs when the beryllate ion forms and what spatial configuration does this correspond to?

Preparation and Properties of Magnesium Hydroxide. Prepare magnesium hydroxide in a test tube by reacting an alkali solution with a solution of a magnesium salt. Pour the contents of the test tube into three tubes and see how magnesium hydroxide reacts with 10% solutions of an acid, alkali, and ammonium chloride. Write the equations of the reactions. Can magnesium hydroxide be precipitated completely if an ammonia solution is used instead of sodium hydroxide? What type of hydroxides do beryllium and magnesium hydroxides belong to? Write the equations of the beryllium and magnesium hydroxide dissociation reactions.

CARBONATES

Beryllium Basic Carbonate. Add a saturated ammonium carbonate solution dropwise to 4-5 ml of beryllium sulphate. Explain the precipitation of a substance and its dissolution in an excess amount of the reactant. Write the equations of the reactions. Boil the solution. Explain the appearance of a precipitate when the solution is boiled. What is its composition?

Magnesium Basic Carbonate (Magnesia Alba). Add a sodium carbonate solution to a magnesium sulphate or chloride solution heated to 50 °C up to complete precipitation. What is the composition of the precipitate? Filter off the latter, wash it with water, and dry it in a drying cabinet at 100-150 °C. Heat the filtrate up to boiling. What do you observe? Write the equations of the reactions.

What reactions occur consecutively in solutions of beryllium and magnesium salts when carbonate ions are introduced into them? In what processes are beryllium and magnesium hydroxo-ions formed? How can normal magesium carbonate be prepared?

BERYLLIUM OXYACETATE

1. Preparation. (*Perform the experiment in a fume cupboard!*) Transfer a preliminarily weighed precipitate of beryllium basic carbonate or hydroxide obtained in one of the preceding experiments

(take it from the laboratory assistant) into a porcelain bowl. Put the latter in a boiling water bath. When the carbonate is hot, add to it preliminarily frozen out glacial acetic acid dropwise until the evolution of carbon dioxide stops (take 2 ml of acetic acid per gramme of the carbonate). Evaporate the solution until dry and repeat the treatment of the residue with acetic acid. Cool the bowl with the substance in a bath with ice. Recrystallize the preparation from chloroform. Filter off the substance that has not dissolved in the chloroform through a dry filter (why?). Pour the filtrate into a porcelain bowl. After evaporation of the chloroform, examine the shape of the crystals obtained under a microscope. What is the composition and structure of beryllium oxyacetate? Write the equation of the reaction.

2. **Sublimation.** (*Perform the experiment in a fume cupboard!*) Put the beryllium oxyacetate crystals into a test tube. Slightly tilt the tube with its mouth downward and carefully heat it in the flame of a burner. What happens? What is the composition of the substance deposited on the tube walls? Examine the crystals of the precipitated and sublimed beryllium oxyacetate under a microscope. What can this compound be used for in the technology of beryllium?

MAGNESIUM AMMONIUM PHOSPHATE

Pour 3-4 ml of a magnesium chloride solution into a test tube and add an ammonia solution. What happens? Add a saturated ammonium chloride solution dropwise until the precipitate dissolves. How can the dissolution of the precipitate be explained? Introduce into the test tube 1 ml of a sodium phosphate solution. What do you observe? Examine the shape of the crystals under a microscope. What is the composition of the crystals? Explain the processes that occur. Write the equations of the reactions. Pour hydrochloric acid into the test tube with the crystals. Explain the dissolving of the precipitate.

20.2 CALCIUM, STRONTIUM, BARIUM

How can the oxides, peroxides, and hydroxides of the alkaline-earth metals be prepared? What are the commercial names of calcium and barium hydroxide solutions? How do the solubility, basic properties, and thermal stability of the hydroxides change in the series calcium-strontium-barium?

Indicate the salts of calcium, strontium, and barium that are poorly soluble. How can you prove experimentally which of the calcium salts is the least soluble? How does calcium oxalate react with acetic and hydrochloric acids? How and why does the thermal

stability of carbonates, sulphates, and nitrates of the alkaline-earth metals change in the series calcium-strontium-barium? What products are obtained if calcium sulphate crystallohydrate is gradually heated?

SUPPLEMENTARY EXPERIMENTS AND SYNTHESES

(Hand in all prepared substances to your instructor.)

1. Preparation of Barium Peroxide. Weigh (with an accuracy up to 0.01 g) about 1 g of barium oxide in a porcelain boat. Place the latter into a porcelain tube and while passing a stream of dry oxygen through the arrangement, roast the barium oxide in a tubular furnace at 600 °C during one hour. Cool the arrangement in the oxygen stream. Extract the boat and weigh it. Calculate the barium peroxide content in the substance prepared in the boat (in per cent). How can you verify that the substance is barium peroxide? Write the equations of the reactions.

2. Preparation of Calcium Hydride. (*Perform the experiment in the presence of your instructor, wear eye protection or a protective mask!*) Assemble an apparatus (see Fig. 115). To produce hydrogen, charge a large Kipp gas generator, using an adequate amount of acid. See that the hydrogen evolves vigorously. Pour an acidified potassium permanganate solution into wash bottle *1* and a 96% sulphuric acid solution into wash bottle *2*. Fill the U-tube with a mixture of glass wool and phosphoric anhydride. Fit an asbestos sleeve onto quartz tube *5* and a rubber tube with a clamp onto the gas-discharge tube at the end of the apparatus. Thoroughly check the tightness of the apparatus (*in the presence of your instructor!*).

Put not more than 1-2 g of freshly cut metallic calcium shavings into iron or porcelain boat *4*, place the latter into the middle of reaction tube *5*, and again test the tightness of the apparatus (*in the presence of your instructor!*).

Open clamp *6* and displace the air from the entire apparatus with a stream of hydrogen. Collect the hydrogen under water to test its purity. Having checked the purity of the hydrogen flowing out of the apparatus, close clamp *6* and completely open the stopcock of the Kipp gas generator (*not a single gas bubble should pass through the wash bottles!*). First heat the entire reaction tube with a gas burner having a flat dovetail nozzle, and then begin heating the tube through the asbestos sleeve at the place where the boat with the metallic calcium is. It is good to hold the gas burner in your hand. The calcium reacts with the hydrogen at a temperature close to 500 °C, and a stream of hydrogen starts passing through wash bottles *1* and *2*. If the reaction proceeds violently, remove the burner and leave the

apparatus under the pressure of the hydrogen. When the absorption of the hydrogen stops (how can this be determined?), cool the apparatus to room temperature in a hydrogen atmosphere. Extract the boat from the tube. What is the colour of the obtained substance? See how calcium hydride reacts with water. Write the equation of the reaction.

3. Preparation of Magnesium Chloride Hexahydrate. Pour 50 ml of a 20% hydrochloric acid solution into a 100-ml beaker and spill the calculated amount of magnesium oxide into the solution in small portions. If the solution is not transparent, filter it. Evaporate the solution to half of its initial volume, place it into a cooling mixture (ice with sodium chloride), and pass a stream of dry hydrogen chloride through it. Filter off the precipitated crystals, dry them on glass at room temperature, and weigh them. Determine the yield in per cent.

Put a small amount of the magnesium chloride hexahydrate into a crucible and roast it. What is observed? Decompose the salt completely. How can you see that this has occurred? Cool the crucible and add 1-2 ml of water. What is the composition of the substance that has not dissolved in the water?

4. Preparation of Anhydrous Magnesium Chloride. *a.* Thoroughly stir magnesium chloride hexahydrate with ammonium chloride, (take the substances in a proportion of 1 : 2 by mass, respectively), put the mixture into a crucible, and roast it in the flame of a gas burner. Cool the crucible in a desiccator (why?).

b. Assemble an apparatus for preparing metal chlorides (see Fig. 61) and check its tightness. Weigh 1 g of freshly cut magnesium shavings in a preliminarily weighed porcelain boat. Put the latter into the quartz or refractory glass tube of the apparatus. Dry the system during 15-20 minutes in a stream of dry carbon dioxide (from a Kipp gas generator), next fill the entire apparatus with chlorine, and heat the part of the tube where the boat is with the flame of a gas burner. When the reaction begins, remove the burner while passing an intensive stream of dry chlorine through the apparatus. If the reaction does not proceed to the end, again heat the magnesium until it ignites. Cool the apparatus in a chlorine stream and displace the chlorine with dry carbon dioxide. Without stopping the carbon dioxide stream, transfer the obtained substance into a weighed dry weighing bottle. Weigh the latter with the substance and calculate the yield in per cent. Pour 3-5 ml of water into a small beaker and introduce a small amount of the magnesium chloride obtained. What do you observe? Write the equations of the reactions.

5. Preparation of Anhydrous Magnesium Chloride by Reacting Hydrogen Chloride with Magnesium in Absolute Ethanol. Assemble an apparatus (see Fig. 116), replacing dropping funnel *2* with a gas-discharge tube. Place 2 g of metallic powdered magnesium into the

three-neck tube and add 50 ml of absolute ethanol to it. Cool the flask in a bath containing a mixture of dry ice and acetone to —70 °C. Pass a stream of thoroughly dried hydrogen chloride through the gas-discharge tube in the side neck of the flask. Saturate the ethanol with the hydrogen chloride while constantly stirring the reaction mixture with the mechanical mixer during 50-60 minutes, then remove the cooling bath and retain a weak hydrogen chloride stream. If the reaction slows down (how can you establish this?), immerse the flask into a water bath at 50-60 °C.

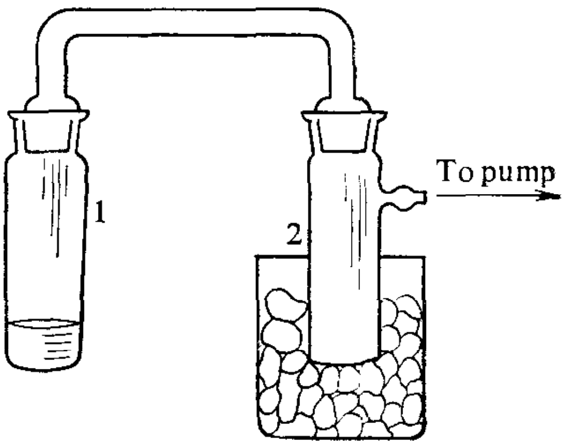


Fig. 118. Arrangement for distilling off a solvent

After termination of the reaction, separate the solution from the unreacted metal by decantation. Transfer the solution into test tube *1* of the arrangement (Fig. 118). Distil off the major part of the ethanol into test tube *2*, heating tube *1* in a water bath. After the substance in tube *1* transforms into a solid mass, connect tube *2* to a water-jet pump and desolvate the product by carefully heating it with the flame of a burner during 40 min. Transfer the substance from the test tube into a previously weighed weighing bottle and weigh it. Calculate the yield in per cent.

6. **Preparation of Magnesium Iodide.** Assemble an apparatus as shown in Fig. 119*a*. Put 2 g of powdered magnesium and 25 ml of absolute ether into three-neck flask *1*. Prepare a solution of 14 g of freshly sublimed iodine and put it into dropping funnel *4*. Switch on mechanical mixer *3*. While vigorously stirring the contents of the flask, add the iodine solution to the reaction mixture from the funnel dropwise. Add each following portion only after the colour produced by the preceding one has disappeared. If the reaction does not begin, carefully heat the reaction mixture in a water bath whose temperature must not exceed 40 °C. (*Use an electric stove with an enclosed coil!*) If the reaction proceeds violently, cool the flask in a bath with ice prepared beforehand.

In 2-2.5 h after termination of the reaction, decant the solution from the unreacted magnesium into a round-bottomed flask (Fig. 119*b*) close it with a stopper provided with a stopcock, and cool it in a bath with dry ice. "Quench" the vacuum created in the flask with argon (nitrogen), using the stopcock of the gas-discharge tube for this purpose. Pour off the mother liquor from the crystals (what is their composition?). If the separated crystals are yellow, recrystallize them from ether. Connect the flask with the crystals to a water-

jet pump. Hold the crystals in vacuum during 30 minutes, after which carefully heat them in a sand bath at 200-226 °C without switching off the pump during 20 minutes (*use an electric stove with an enclosed coil!*). It is better to decompose the adduct in a blackened flask (why?).

Transfer the magnesium iodide crystals into a weighed weighing bottle and weigh them. Calculate the yield in per cent.

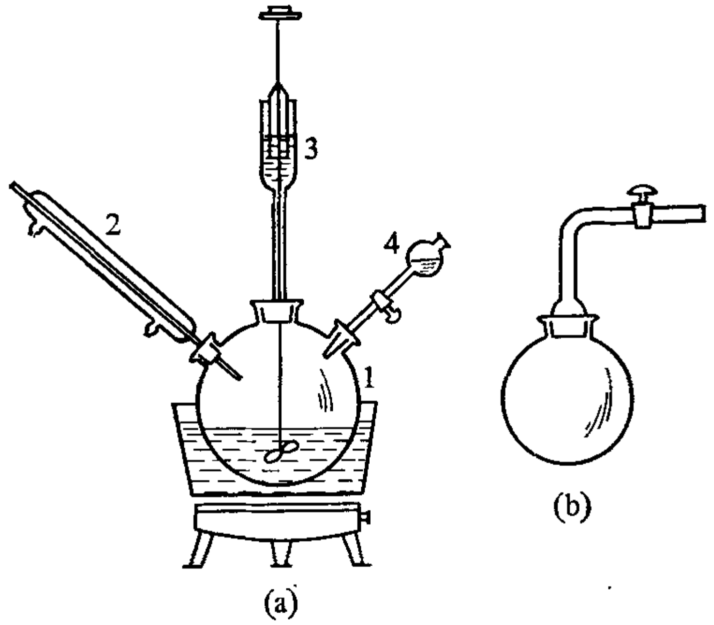


Fig. 119. Apparatus for reacting metallic magnesium (zinc) with iodine in absolute ether (*a*), and flask for distilling off the solvent (*b*)

7. **Preparation of Calcium Chloride Hydrate.** Pour 100-120 ml of a 15% hydrochloric acid solution into a 200-ml beaker. Calculate the amount of marble or chalk needed to convert this amount of acid into calcium chloride. Weigh this amount, crush it, and gradually add it to the acid. If after dissolving of the taken amount of marble the reaction of the solution will be strongly acidic, add more marble. Filter the solution. Evaporate it until the boiling point of the solution reaches 128-129 °C (*use a thermometer*). Using the data of Table 5, calculate the ratio of calcium chloride and water (in moles) in a solution boiling at 130 °C.

Table 5. TEMPERATURE DEPENDENCE OF THE CALCIUM CHLORIDE CONTENT IN A SOLUTION

Boiling point of calcium chloride solntion, °C	Solubility, g per 100 g of water	Boiling point of calcium chloride solution, °C	Solubility, g per 100 g of water
105	25.0	120	69.0
110	41.5	130	101.0

Stop the evaporation and let the solution cool. What do you observe? What is the composition of the precipitating substance? Separate the crystals from the mother liquor on a funnel with a filtering bottom. Examine and draw the shape of the crystals. Determine the yield in per cent.

Weigh about 3-4 g of anhydrous calcium chloride in a weighing bottle and let it stand open in the air for two or three days. Again weigh the bottle with the substance. How can you explain the increase in mass? What is anhydrous calcium chloride used for in the laboratory?

8. **Processing of Barium Sulphate into Barium Chloride.** *a. Preparation of Barium Sulphide.* Mix 4 g of barium sulphate and 2 g of powdered charcoal, place the mixture into a chamotte or porcelain crucible, and cover the mixture with powdered charcoal. Close the crucible with its lid and roast it strongly (600-700 °C) for an hour in a muffle furnace. Write the equation of the reaction.

After the sintered substance has cooled, extract it from the crucible and triturate it in a porcelain mortar. Treat a small part of the triturated substance with water, filter the solution, and test its reaction with litmus. Pass a stream of carbon dioxide through the solution. Note the odour that appears. Explain what happens. Write the equations of the reactions.

b. Preparation of Barium Chloride Hydrate. Pour 20 ml of a 20% hydrochloric acid solution into a porcelain bowl and add the remaining part of the prepared barium sulphide to it in small portion *(in a fume cupboard!)*. Boil the solution to remove the hydrogen sulphide. Write the equation of the reaction. If the solution has an alkaline reaction, neutralize it with hydrochloric acid. If necessary, filter the solution and evaporate it until a sample of the solution begins to crystallize when cooled (put the sample onto a watch glass with a glass rod). Cool the solution. Examine the crystallizing substance under a microscope and draw the shape of the crystals. Filter off the crystals on a Büchner funnel and place them into a small jar with a ground-glass stopper.

9. **Preparation of Magnesium Perchlorate.** Pour together two hot solutions (10 ml each) containing equimolecular amounts of sodium perchlorate and magnesium chloride and saturated at 90 °C. Without letting the liquid cool, filter off the separated crystals on a funnel with a filtering bottom. Why cannot the solution be filtered through a paper filter? What substance crystallizes from the hot solution? What substance precipitates when the mother liquor is cooled? Also filter off the crystals precipitating from the cold solution on a funnel with a filtering bottom. Examine the shape of the crystals of both substances under a microscope.

Transfer the magnesium perchlorate crystals into a porcelain crucible and dehydrate the salt by heating it in a drying cabinet at

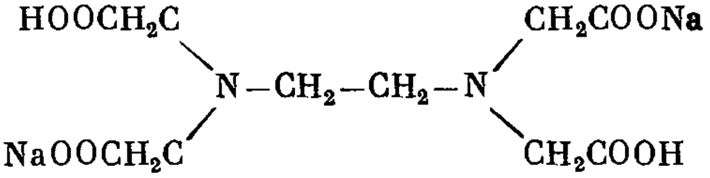
230 °C. How can you make sure that dehydration has terminated? Cool the preparation in a desiccator over calcium chloride and transfer it into a previously weighed dry jar with a good ground-glass stopper. Weigh the jar with the preparation and calculate the yield in per cent.

Put a small amount of the anhydrous salt into a weighing bottle and weigh it with an accuracy up to 0.1 g. Leave the bottle open up to your next lesson and weigh it again. What is the change in the weight of the bottle with the salt due to? What is magnesium perchlorate used for? Why is magnesium perchlorate preferable to other desiccants?

10. Preparation of Magnesia Cement. Dissolve 1 g of magnesium chloride hexahydrate in a minimum amount of water in a porcelain bowl and add an amount of magnesium oxide to the solution such that there are two parts by weight of the magnesium oxide per part by weight of anhydrous magnesium chloride. Put the paste into the lid of a crucible and let it stand up to your next lesson. What happens to the paste? Identify the compound formed. Where is magnesia cement used?

11. Determining the Hardness of Water. The hardness of water in some countries is expressed in units called continental hardness degrees. One degree corresponds to a content of 10 mg of calcium oxide in one litre of water (1 part in 100 000); magnesium oxide is converted to calcium oxide in an equivalent ratio (by multiplying the amount of magnesium oxide by 1.4). In the USSR, the unit of water hardness is a total calcium and magnesium content in it amounting to 1 mg-equiv. per litre of water. One degree of hardness expressed in milligramme-equivalent corresponds to 2.8 continental hardness degrees.

At present, the complexonometric method of determining water hardness is being widely used. This method is very sensitive and simple to use. It is based on the ability of the disodium salt of ethylenedinitrilotetraacetic acid (EDTA or complexon)



to form poorly dissociating complexes with ions of magnesium, and especially of calcium. Oxynitrodyes such as Eriochrome black T are used as an indicator.

This method is used for water with a varying salt content, but with a view to the weakly alkaline reaction in the solution in titration, one should never have a total calcium and magnesium ion concentration in a water sample exceeding 0.5 mg-equiv/litre. There-

fore, when taking water for titration, use the following volumes:

Concentration of calcium and magnesium ions, mg-equiv/litre	0.5-5.0	5-10	10-20	20-50
Volume of water for titration, ml	100	50	25	10

When the water being studied contains no magnesium ions, which occurs very rarely, the determination is possible only when a definite amount of magnesium ions is added to the volume of water measured for titration. This amount must then be subtracted from the results of the determination.

Course of Determination. Transfer with a pipette the required volume of the water being studied into a 200-ml conical flask, add with a measuring glass distilled water up to a total volume of 100 ml, 5 ml of a buffer solution maintaining the pH at about 10, and 4-7 drops of an Eriochrome black T indicator. Stir the liquid, and then titrate with a 0.02 N EDTA solution until the colour changes from violet-red to light blue. (When the total calcium and magnesium content is below 0.5 mg-equiv/litre, use a 0.01 N solution instead of a 0.02 N one to improve the accuracy.) The end of titration will be noticeable better if you place next to it a titrated sample whose colour is used as a reference. When more EDTA is added, the colour and its intensity do not change.

Calculation of Results. The total calcium and magnesium ion content x (in mg-equiv per litre of the water being studied) is calculated by the following formula:

$$x = VN\frac{1000}{v_1}$$

where V is the volume of the EDTA solution used for the determination, N is the normality of the EDTA solution, and v_1 is the volume of water taken for the determination.

Example. In the titration of 50 ml of water being studied (plus 50 ml of distilled water), 12.55 ml of an EDTA solution with a normality of 0.0203 were used. Hence, the total content of calcium and magnesium ions will be

$$x = 12.55 \times 0.0203 \times \frac{1000}{50} = 5.10 \text{ mg-equiv/litre}$$

12. Solutions Used in Hardness Determination. *Standard Solution.* It is prepared from a mixture of 0.1 N solutions of calcium and magnesium salts in the ratio 3 : 1.

Gradually heat a chemically pure preparation of magnesium sulphate heptahydrate in a drying cabinet to 250 °C, bringing it up to a constant weight. After cooling in a desiccator, weigh 3.0088 g of

anhydrous magnesium sulphate, dissolve it in distilled water in 500-ml measuring flask, and bring its volume up to the mark on the flask.

Dry a chemically pure preparation of calcium carbonate in a drying cabinet at 110 °C and after cooling in a desiccator, weigh 5.004 g. Transfer the substance into a one-litre measuring flask, add about 10 ml of distilled water and then concentrated hydrochloric acid dropwise, avoiding an excess (usually about 8-9 ml are needed) up to complete dissolution of the calcium carbonate. Pour in distilled water up to the mark on the flask.

To prepare a 0.02 *N* standard solution of calcium and magnesium salts, pour 75 ml of a 0.1 *N* calcium chloride solution and 25 ml of a 0.1 *N* magnesium sulphate solution into a 500-ml measuring flask, and then add distilled water up to the mark on the flask.

EDTA Solution. Prepare a 0.02 *N* EDTA solution by dissolving 3.75 g of EDTA (complexon) in distilled water in a one-litre measuring flask and then bring the volume up to the mark on the flask.

Determining the Normality of the EDTA Solution. Transfer 15 ml of the 0.02 *N* standard calcium and magnesium solution with a pipette into a 200-ml conical flask, and add 85 ml of distilled water and 5 ml of a buffer solution. Stir the liquid and add 4-7 drops of an indicator solution, after which titrate it with EDTA in the same way as when determining calcium and magnesium. Calculate the normality N of the EDTA solution by the formula

$$N = N_1 \frac{a}{V}$$

where a is the taken amount of the standard calcium and magnesium solution, ml, N_1 is the normality of this solution, and V is the amount of the EDTA solution used in titration, ml.

Buffer Solution. Dissolve 20 g of chemically pure ammonium chloride in distilled water, add 100 ml of a concentrated ammonia solution, and add distilled water up to one litre.

Solution of Eriochrome Black T Indicator. Dissolve 0.5 g of a chemically pure preparation in 10 ml of the buffer solution and add ethanol up to 100 ml. Other oxynitrodyes can be used in addition to Eriochrome black T.

21 ALUMINIUM

Indicate the position of aluminium in Mendeleev's periodic table of the elements, the electron configuration, size of its atom, and its oxidation states.

21.1 PROPERTIES

What place is occupied by aluminium in the electrochemical series of the metals? How does it react with dilute and concentrated solutions of acids (hydrochloric, sulphuric, nitric) in the cold and when heated, does it react with alkali solutions? Write the equations of the reactions.

Reaction of Aluminium with Oxygen and Water. (The experiment is prepared by one student who demonstrates it to the class.) Clean two aluminium plates from aluminium oxide with emery paper and next from grease by boiling them in a small amount of ethanol. Put the plates into a porcelain bowl in a tray with high sides and pour a few drops of a mercury(II) nitrate solution onto them. After five minutes, wash the plates with water, put one of them on a watch glass, and leave it in the air. Immerse the other one into a beaker with water. Observe what occurs and explain these phenomena. Write the equations of the reactions.

21.2 COMPOUNDS

ALUMINIUM HYDROXIDE

Prepare aluminium hydroxide (what methods can be used for this purpose?). Wash the precipitate by decantation and treat it with: (a) a sulphuric acid solution, (b) an excess of a sodium hydroxide solution, and (c) an excess of an ammonia solution. What do you observe? Write the equations of the reactions. How can solid sodium aluminate be prepared?

POTASSIUM ALUMINIUM ALUM

Prepare hot saturated solutions of aluminium and potassium sulphates. To do this, dissolve 6.66 g of aluminium sulphate crystallohydrate in 5 ml of hot ($\sim$70 °C) water. Calculate what amount of potassium sulphate is equimolecular to 6.66 g of the aluminium sulphate crystallohydrate. Weigh this amount of potassium sulphate and dissolve it in 10 ml of hot water. Pour the potassium sulphate solution into that of aluminium sulphate. Cool the solution, filter off the precipitated crystals, dry them between sheets of filter paper, weigh them, and determine the yield of the substance in per cent. Examine the shape of the crystals under a microscope and draw them.

OTHER COMPOUNDS

How can the crystallohydrates of aluminium sulphate and aluminium chloride be prepared? How does the colour of indicators (methyl red, litmus) change in solutions of aluminium sulphate

and of sodium aluminate? Which of these salts hydrolyzes to a greater extent and why? What aluminium compound precipitates if (a) a sodium carbonate solution is added to a solution of an aluminium salt, and (b) a stream of hydrogen sulphide is passed through a solution of an aluminium salt?

SUPPLEMENTARY EXPERIMENTS AND SYNTHESES

(Hand in all the preparations to your instructor.)

1. **Preparation of Iron by Aluminothermic Process.** Roast iron oxide in an iron crucible (for what purpose?). Prepare a mixture of 25 g of the iron oxide and 8 g of an aluminium powder. Place 5 g of a calcium fluoride powder, and then the reaction mixture onto the bottom of a well dried chamotte crucible (a crucible can be made from a sheet of asbestos by fastening it with a wire). Tamp the contents with a pestle and make a hollow in them with the aid of a test tube (Fig. 120). Extract the tube and lower into the formed hollow first a twisted magnesium ribbon cleaned with emery paper, and then an incendiary mixture prepared by mixing 9 g of barium peroxide and 1 g of a magnesium powder in a jar *(Never grind the incendiary mixture in a mortar!)*.

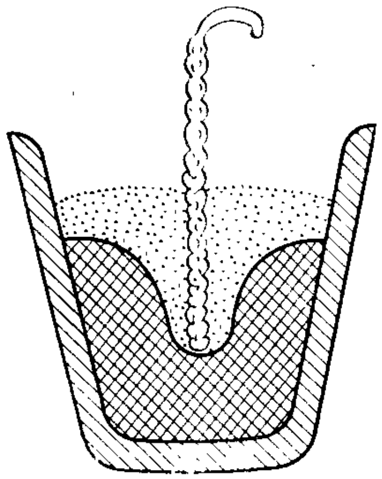


Fig. 120. Chamotte crucible for an aluminothermic process

Put the crucible into a metal bath with dry sand so that the crucible is submerged in the sand up to one-third of its height. (*Perform the experiment in a fume cupboard behind a glass window in the presence of your instructor! Wear eye protection or a protective mask!*) Ignite the ribbon with a burning splinter inserted into a long glass tube serving as a handle. What happens? *Do not look into the crucible if the reaction is delayed somewhat!*

After the crucible cools, break it, extract the metal bead, and weigh it. Determine the yield in per cent. Write the equation of the reaction.

2. **Preparation of Aluminium Hydroxide.** Weigh 0.5 g of metallic aluminium and dissolve it in a calculated amount of a 10% alkali solution. Filter the liquid from undissolved impurities and divide it into two unequal parts. Pass a stream of carbon dioxide through the larger part of the filtrate. Explain what occurs. Heat the smaller

part of the solution up to boiling and add a few millilitres of a saturated ammonium chloride solution. What is observed? Write the equation of the reaction. Wash the precipitate several times with water by decantation, filter it off, and dry it in a cabinet, gradually raising the temperature to 100 °C.

3. **Preparation of Sodium Aluminate.** Weigh 0.5 g each of finely ground aluminium oxide and anhydrous sodium carbonate, thoroughly mix them, and spill them into an iron crucible. Put the latter on a porcelain triangle and heat it strongly with the flame of a brazing burner until carbon dioxide stops evolving. Cool the crucible, extract the fused substance, and grind it in a mortar. Transfer a small part of the substance into a beaker and pour water over it. Test the solution with an indicator. What do you observe? Write the equations of the reactions. How can aluminium hydroxide be precipitated from an aluminate solution.

4. **Preparation of Aluminium Sulphate from Kaolin.** Roast about 25 g of kaolin with the access of air in a muffle furnace (800 °C) to remove the moisture and oxidize organic matter. Weigh the roasted substance, thoroughly mix it with the calculated amount of a 40% sulphuric acid solution, and heat it at 200 °C in a sand bath during three or four hours.

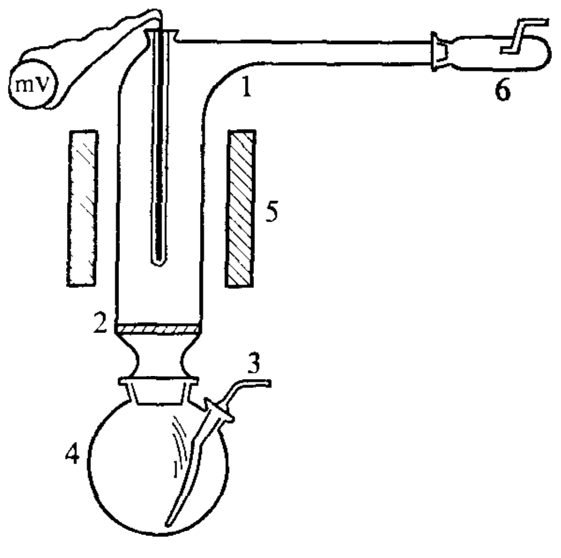


Fig. 121. Apparatus for preparing metal chlorides in a fluidized bed

Treat the product with hot water, filter the solution, and evaporate it until crystals form. Let the cooled solution stand for crystallization. Pour a drop of the hot saturated solution onto a slide, examine the formed crystals under a microscope, and draw their shape. Filter off the obtained salt on a Büchner funnel, dry it in the air, and weigh it. What is the composition of the salt? Write the equation of the reaction. Calculate the yield in per cent. Roast a small part of the crystals on the lid of a crucible. Explain what you observe.

5. **Preparation of Aluminium Chloride in a Fluidized Bed.** Assemble an apparatus as shown in Fig. 121. Place 25 g of dry aluminium oxide onto porous chamotte partition *2* of quartz reactor *1* and 200-250 ml of carbon tetrachloride into flask *4*. Pass a stream of dry nitrogen into the apparatus via tube *3* at such a rate that a "flame" of the metal oxide appears at a distance of 30-50 mm from the edge of the horizontal bend of the reactor.

Switch on furnace *5* and raise the temperature in the reactor up to 850-900 °C. Heat the carbon tetrachloride in a water bath up to

60-65 °C. If a blue or blue-black colour appears in receiver *6* (explain its origin), lower the evaporation temperature of the carbon tetrachloride to 50 °C. Perform chlorination during 15 minutes.

After completing chlorination, disconnect receiver *6* with the sublimed product and rapidly transfer it into a dry chamber or a large desiccator filled with dry carbon dioxide. Spill the obtained substance into a weighed drawn out test tube and seal the latter. Weigh the ampoule with the substance and the remaining part of the tube. Calculate the yield in per cent.

6. Preparation of Aluminium Bromide. (*Perform the experiment in a fume cupboard!*) Assemble an apparatus as shown in Fig. 122*a*.

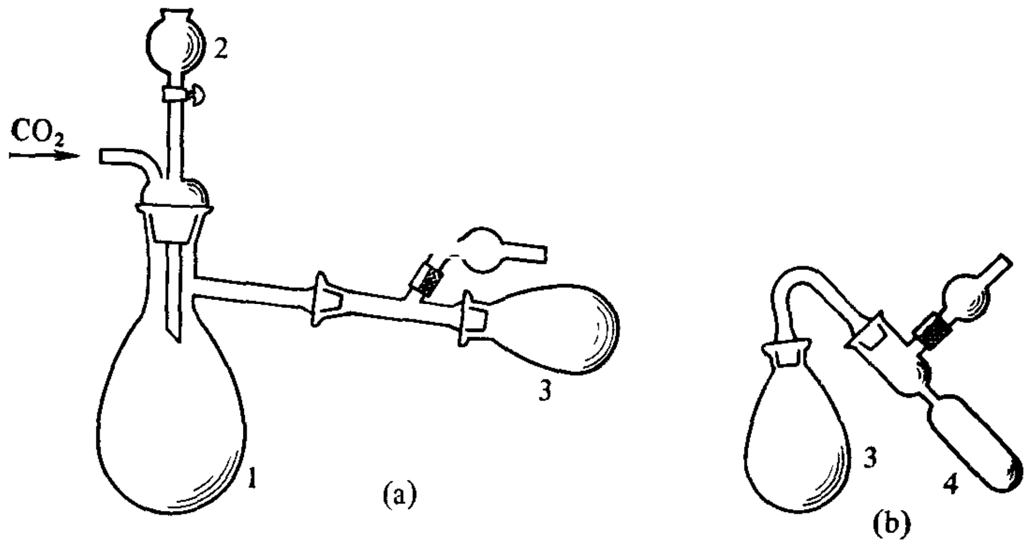


Fig. 122. Apparatus for preparing aluminium bromide

Lubricate the ground-glass joints in the apparatus with a concentrated sulphuric acid solution. Clean a piece of metallic aluminium with emery paper, make 10-12 g of shavings from it, and put it into flask *1*. Pour 30 ml of dry bromine into dropping funnel *2*. This amount of bromine is not sufficient for the aluminium to enter into the reaction completely (why is excess aluminium taken?)

While heating flask *1* with a small burner flame, dry the apparatus with a stream of carbon dioxide thoroughly dried by passing it consecutively through two wash bottles with concentrated sulphuric acid and a column with phosphorus pentoxide. Add the bromine dropwise to the aluminium. At the beginning of the experiment, carefully heat the flask containing the aluminium with the flame of a burner; when the contents of the flask have been heated strongly, stop the heating.

After termination of the reaction, heat flask *1* strongly with the flame of a burner and distil the obtained aluminium bromide in a stream of carbon dioxide into receiver *3*. To remove traces of bromine, repeat the distillation in the apparatus shown in Fig. 122*b*

putting several pieces of metallic aluminium into it (for what purpose?). Collect the aluminium bromide in weighed receiver *4* cooled with a mixture of ice and sodium chloride. When the distillation is completed, disconnect the receiver (a Wurtz test tube) from the apparatus and seal it at the narrow part. Weigh the sealed ampoule with the preparation and the remaining part of the test tube. Calculate the yield in per cent proceeding from the taken amount of bromine.

22 THE RARE-EARTH ELEMENTS

Indicate the position of the rare-earth elements in Mendeleev's periodic table, the electron configurations and sizes of their atoms, and their oxidation states.

22.1 CERIUM(III) COMPOUNDS

HYDROXIDE

1. Pour 1 ml of cerium nitrate into a test tube and add a few drops of sodium hydroxide. What happens? Write the equation of the reaction. Act on the precipitate with an excess amount of the sodium hydroxide. Does cerium hydroxide react with sodium hydroxide?
2. React the cerium hydroxide precipitate with 1 *N* solutions of hydrochloric, sulphuric, and nitric acids. Write the equations of the reactions.
3. Prepare cerium(III) hydroxide as described above and let it stand in the air. In a few hours, note what changes occurred in the precipitate. Write the equation of the reaction.
4. Add a hydrogen peroxide solution to a cerium(III) hydroxide precipitate. How does the colour of the precipitate change? Write the equation of the reaction.

SALTS

1. Add a sodium carbonate solution to a cerium nitrate one. What do you observe? Write the equation of the reaction. How do mineral acids react with the obtained salt?
2. Prepare cerium oxalate and see how it reacts with acids. What is the value of the solubility product of cerium oxalate?

22.2 CERIUM(IV) COMPOUNDS

HYDROXIDE

1. Pour a sodium hydroxide solution into a solution of cerium(IV) sulphate. What is observed? Write the equation of the reaction.
2. Add an equal volume of a sodium carbonate solution to a cerium nitrate one, next add dropwise a potassium permanganate solution. What is the composition of the precipitate? Write the equation of the reaction.

SALTS

1. Add an ammonium persulphate solution to one of cerium(III) sulphate. What changes do you observe? Write the equation of the reaction.
2. Add a potassium iodide solution to one of cerium(IV) sulphate acidified with sulphuric acid. How can you explain the change in the solution's colour? Write the equation of the reaction. What properties do cerium(III) and cerium(IV) salts exhibit?

SUPPLEMENTARY EXPERIMENT

Preparation of Cerium(III) Sulphate by the Photochemical Reduction of Cerium(IV) Compounds with Ethanol. Place 6 g of cerium(IV) nitrate into a wide 150-ml beaker and dissolve it in a minimal amount of water. Add 20 ml of 50% sulphuric acid and 20 ml of ethanol to the solution. Irradiate the mixture with ultraviolet light up to the complete vanishing of the orange colour, maintaining a constant volume in the beaker by adding ethanol. Next evaporate the solution in a water bath, retaining a small volume of the mother liquor. Rapidly, without letting the solution cool, separate the colourless crystals with the aid of a glass filter No 2 ($\sim$ 270 mesh). Dry the crystals in the air, place them in a weighed glass weighing bottle, weigh them, and calculate the yield in per cent.

23 TITANIUM, ZIRCONIUM, HAFNIUM

Indicate the position of titanium, zirconium, and hafnium in Mendeleev's periodic table of the elements, the electron configurations and size of their atoms, and their oxidation states.

What places are occupied by these metals in the electrochemical series? How do they react with the oxygen of the air, with water, acids, and alkalies?

23.1 TITANIUM(IV) COMPOUNDS

Titanic Acid. Add a 10% ammonia solution to 10 ml of a solution of titanium tetrachloride in hydrochloric acid with constant stirring up to the complete precipitation of titanic acid. Let the precipitate settle, pour off the solution, and rinse it several times with water by decantation.

See how titanic acid reacts with 10% solutions of acids and alkalies. Shake a small amount of titanic acid in a test tube with water and boil it. Pour off the water and again see how the titanic acid reacts with acids and alkalies. How and why did the reactivity of the titanic acid change?

Put a small amount of the titanic acid on the lid of a crucible, dry it in a drying cabinet, and then roast it. What is obtained? Write the equation of the reaction. How does the colour of the preparation change when roasted? Is the previous colour restored after the substance has been cooled? Dry the remaining amount of the titanic acid in the air and hand it in to the laboratory assistant.

What hydrates are called alpha- and beta-titanic acids, how are they prepared, and what are their properties? How, having at hand titanium(IV) oxide, can you prepare potassium titanate and titanyl sulphate?

Compare the properties of titanium(IV), zirconium(IV), and hafnium(IV) hydroxides.

Hydrolysis of Titanium Tetrachloride. (*Perform the experiment in a fume cupboard!*) Pour 4-5 ml of water into a bowl and add a few drops of titanium tetrachloride. What is observed? Write the equation of the reaction.

Peroxide Compounds. Add a few drops of a 3% hydrogen peroxide solution to a solution of titanium tetrachloride in hydrochloric acid. What do you observe? What is the composition of titanium peroxide compounds?

23.2 TITANIUM(III) COMPOUNDS

Preparation of Titanium(III) Sulphate Solution. Pour 7-10 ml of an acidified titanyl sulphate solution into a test tube, add 3-5 ml of a 10% sulphuric acid solution, and put in two or three small pieces of zinc. How does the colour of the solution change? Write the equation of the reaction.

Studying the Properties of Titanium(III) Compounds. Pour 2 ml of the titanium(III) sulphate solution prepared in the preceding experiment into each of two test tubes. Let one tube stand in the air. What is observed? Add several drops of a potassium permanganate solution to the other tube. What happens? Write the equations of the reactions.

Pour the remaining titanium(III) sulphate solution off the zinc into a third test tube and rapidly add to it a 10% sodium hydroxide solution. See how titanium(III) hydroxide reacts with the oxygen of the air, and also with 10% acid and alkali solutions. Write the equations of the reactions. What properties do titanium(III) compounds exhibit?

Why do titanium(III) salts hydrolyze to a smaller extent than titanium(IV) salts? Using the crystal field theory, explain why titanium(III) compounds are coloured, while titanium(IV) ones are colourless.

SUPPLEMENTARY EXPERIMENTS

(Hand in all obtained preparations to your instructor.)

1. **Preparation of Titanium Tetrachloride and Studying of Its Properties.** *a. Preparation.* (*Perform the experiment in a fume cupboard!*) Weigh 5 g of titanium(IV) oxide, 2 g of powdered coal, 2 g of dextrin, and thoroughly mix them. Wet the mixture with a small amount of water and, while stirring it with a glass rod, prepare beads the size of a pea from it. Put the beads on a ceramic dish, and dry them first in the air and then in a drying cabinet at 150-200 °C during three to five hours. Carefully transfer the beads into a crucible and cover them with a layer of powdered coal. Cover the crucible with its lid or a piece of asbestos and roast it in a muffle furnace at 500-600 °C during 30-40 minutes.

Cool the beads in a desiccator and rapidly transfer them into the quartz tube of a chlorination apparatus (see Fig. 111). Again dry the mixture in a stream of clean and dry carbon dioxide at 500-600 °C until steam stops condensing at the quartz tube outlet. After removal of the moisture, connect a preliminarily weighed receiver—a Wurtz flask or a Wurtz test tube—to the reaction tube instead of flask *3*. Displace the carbon dioxide with a stream of dry chlorine and, maintaining the furnace temperature at about 600 °C, pass a strong chlorine stream through the system. What happens? Write the equation of the reaction.

When condensation of the titanium tetrachloride ends, cool the furnace to 200-300 °C without stopping the chlorine stream, then displace the chlorine with a stream of dry carbon dioxide, rapidly remove the receiver flask, and close it with a preliminarily weighed stopper. Weigh the receiver with the titanium tetrachloride and calculate the yield in per cent.

Pour part of the titanium tetrachloride into a small beaker containing 5-10 ml of concentrated hydrochloric acid. What occurs? Write the equation of the reaction. Remove the stopper from the receiver flask. Lower a few copper shavings into the flask (for what purpose?) and capillaries sealed at one end. Rapidly close the flask with a stop-

per provided with a dephlegmator and a thermometer (see Fig. 20). Cover the flask with asbestos and put it onto an electrical flask heater. What is the boiling point of titanium tetrachloride? Distil the titanium tetrachloride into a test tube provided with a constriction and cooled with dry ice, and seal the tube (*wear eye protection, seal the tube in the presence of your instructor!*).

b. Hydrolysis. (*Perform the experiment in a fume cupboard!*) Pour 4-5 ml of water into a bowl and add several drops of titanium tetrachloride (a laboratory preparation). Comment on your observations.

2. Preparation of Zirconium (Hafnium) Bromide (Iodide). To prepare a zirconium (hafnium) halide, use a multisection tube made from refractory glass with a test tube and offtake fused to it (Fig. 123).

When preparing zirconium bromide, place 1-2 g of phosphoric anhydride into test tube *1* and through offtake *2* pour in the amount of

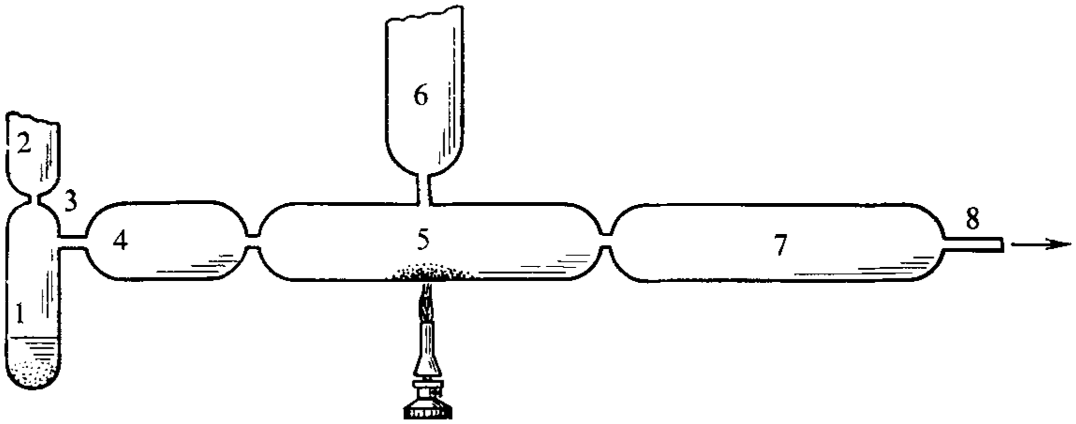


Fig. 123. Apparatus for preparing zirconium (hafnium) halides

bromine calculated for reacting with 3 g of metallic zirconium. Dry the bromine beforehand over phosphorus(V) oxide.

When preparing zirconium iodide, take 20% less iodine than the stoichiometric amount. Place the iodine into test tube *1* and spill a mixture of potassium iodide and freshly prepared calcium oxide (2-3 g) onto it.

Seal off offtake *2* and spill metallic zirconium into section *5* via offtake *6*. Tightly close offtake *6* with a rubber stopper. Connect the apparatus via offtake *8* to a vacuum system for 15-20 min. Next place test tube *1* into a Dewar vacuum flask with liquid nitrogen and seal off offtake *6*. (*Perform this work wearing eye protection in the presence of your instructor!*) After the pressure in the system becomes equal to 10^{-2} mmHg (in about 40-60 minutes), seal off offtake *8*. Stop cooling test tube *1* and wait until the apparatus acquires room temperature.

Fasten the sealed apparatus in a stand behind the protective window of a fume cupboard (*wear eye protection!*) and slightly heat

the section containing the metal with a burner. Carefully heat test tube *1* with a burner until the halogen begins to evaporate. After the reaction starts, stop heating the zirconium. Make sure that section *7* remains cold and the constrictions between the sections are not clogged with the product.

When a violent reaction stops, heat the metal again. After evaporation of all the halogen from test tube *1*, seal off constriction *3* very carefully. Repeatedly pass the halogen over the heated metal. When the halogen vapour disappears in the apparatus, distil the product into section *4* or *7* and seal it off.

3. The Preparation of Ammonium Heptafluozirconate(IV). In a platinum bowl, dissolve 20 g of zirconium(IV) oxide in a hot 40% hydrogen fluoride solution taken in an excess of 20% relative to the calculated amount needed to convert the zirconium(IV) oxide to the tetrafluoride. Cool the solution in a bath with ice to 5 °C and filter it through a paper filter (preliminarily cover the funnel with a thin layer of paraffin).

Calculate the amount of ammonium fluoride needed to convert the zirconium tetrafluoride to ammonium heptafluozirconate, and weigh a three-fold excess of the substance (why should the excess ammonium fluoride be taken?). Dissolve the ammonium fluoride in a minimum amount of water (see Appendix 1, Table 1), filter the solution, and add it to the zirconium tetrafluoride solution. If no ammonium heptafluozirconate precipitate appears, add 10-20 ml of ethanol. Filter off the precipitate with the aid of a Büchner funnel, rinse it several times on the filter with ethanol, and dry it in the air.

It is good to perform all the operations in platinum ware. Transfer the product into a weighed weighing bottle and weigh it. Calculate the yield in per cent. Ammonium heptafluohafnate can be prepared in a similar way.

24 VANADIUM, NIOBIUM, TANTALUM

Indicate the position of vanadium, niobium, and tantalum in Mendeleev's periodic table of the elements, the electron configurations and size of their atoms, and their oxidation states.

What place do these metals occupy in the electrochemical series? How do they react with acids and alkalies? What compounds form when vanadium, niobium, and tantalum react with oxygen, the halogens, and sulphur?

24.1 VANADIUM COMPOUNDS

Preparation of Vanadium(V) Oxide. Put 0.1-0.2 g of ammonium vanadate onto the lid of a crucible. Heat the lid with the flame of a burner through an asbestos gauze. What do you observe? Write the equation of the reaction.

Properties of Vanadium(V) Oxide. Put a small amount of vanadium(V) oxide into a number of test tubes. See how it reacts with water, 10% solutions of hydrochloric, sulphuric, and nitric acids, and also of an alkali in the cold and when heated. Write the equation of the reactions.

What is the value of the solubility of vanadium(V) oxide in water? What ions are present in an aqueous solution of vanadium(V) oxide and what crystallohydrates of this oxide have been separated? How do the oxidizing properties of vanadium(V) oxide manifest themselves?

Salts of Vanadic Acid. Pour 3-4 ml of a sodium vanadate solution into each of two test tubes. Add to one of them a silver nitrate solution, and to the other a saturated ammonium chloride solution. Write the equations of the reactions.

Add a 1 *N* sulphuric acid solution dropwise to a sodium vanadate solution with stirring. Explain the change in the colour of the solution. Write the net ionic equations of the reactions proceeding in an aqueous solution of vanadates when the pH decreases or increases.

Vanadium Peroxide Compounds. Add several drops of a 3% hydrogen peroxide solution to 2-3 ml of a sodium vanadate solution acidified with a dilute sulphuric acid solution. What is observed? Write the equation of the reaction.

Compounds of Vanadium in Lower Oxidation States. Melt paraffin in a porcelain bowl or test tube. Put seven test tubes with stoppers onto a test tube stand. Pour 10 ml of a sodium vanadate solution into a small 50-ml flask, add 10 ml of a 20% sulphuric acid solution, and put in 8-10 small pieces of granulated zinc. Watch how the solution's colour changes. As a new colour appears, pour off 1-2 ml of the solution into each of three of the tubes. In one of them, pour melted paraffin over each layer of liquid with a new colour. Close the other two tubes with their stoppers and pour the following portion of the solution with a new colour into two empty tubes with stoppers.

What vanadium compounds are obtained when zinc reacts with a sodium vanadate solution in an acid medium? Write the equations of the reactions.

Rapidly add a 10% sodium hydroxide solution to one series of solutions containing compounds of vanadium in different oxidation states. What do you observe? See how the obtained hydroxides react with acids and alkalies. Add a potassium permanganate solution

dropwise to another series of solutions having the corresponding colour. What do you observe? Let the flask with the remaining part of the solution stand open in the air and watch how the solution's colour changes. Write the equations of the reactions.

SUPPLEMENTARY EXPERIMENTS AND SYNTHESES

(Hand in all the obtained preparations to your instructor.)

1. Preparation of Vanadium by the Aluminothermic Process. (*Perform the experiment in the presence of your instructor! Wear eye protection or a protective mask!*) Thoroughly dry vanadium oxide in a drying cabinet at 120-130 °C. Prepare a mixture of 10 g of vanadium(V) oxide with 6.5 g of aluminium in grains. Place the mixture into a chamotte crucible as shown in Fig. 120.

Prepare 16 g of an incendiary mixture (see p. 202). Insert a magnesium ribbon into the hollow made with a test tube and spill the incendiary mixture into the hollow. Place the crucible into a bath with sand. Perform the experiment on the floor near a fume cupboard or in one. Carefully ignite the magnesium ribbon with a burning splinter inserted into a long glass tube. After the flash, let the molten substance cool, break it up, and extract the metal bead.

How does vanadium react with acids and alkalies?

2. Preparation of Vanadium(V) Oxide. Weigh 0.5 g of ammonium vanadate in a crucible. Roast the crucible with its contents up to a constant mass in a crucible furnace at 300-400 °C. Roast in an atmosphere of dry oxygen or air, feeding it into the furnace from a gas meter. Why is the substance roasted in an oxygen atmosphere? Write the equation of the reaction.

Study the properties of vanadium(V) oxide (see p. 211).

3. Preparation of Sodium Vanadate. Put a thoroughly triturated mixture of 0.5 g of vanadium(V) oxide and 1 g of sodium carbonate into a crucible and place it into a crucible furnace. Raise the furnace temperature to 800 °C and control the course of the process. Lower the hot crucible into a beaker with water to separate the melt easily from the crucible walls. Crush the melt in a mortar and treat it with water while heating. Evaporate the solution until crystallization begins. Examine the crystals under a microscope. Write the equation of the reaction.

Study the properties of vanadates (see p. 211).

4. Preparation of Vanadium Oxychloride and Studying of Its Properties. *Preparation of Vanadium Oxychloride by Roasting a Mixture of Vanadium(V) Oxide with Charcoal in a Chlorine Stream.* Prepare a fine mixture of 5 g of vanadium(V) oxide, 3 g of charcoal, and 5 g of dextrin. Add water dropwise to the mixture until a paste

forms. Prepare beads the size of a pea from it. Place the beads on a ceramic dish and dry them in a drying cabinet at 150-200 °C, next transfer them into a crucible, and spill charcoal over them. Cover the crucible with its lid or a piece of asbestos and roast it in a muffle furnace at 600-700 °C. Cool the beads in a desiccator and transfer them into the reaction tube of a chlorination apparatus (see Fig. 111).

Switch on the furnace and, without connecting receiver *2*, dry the beads again in a carbon dioxide atmosphere at 500-600 °C. When the evolution of moisture stops, connect weighed receiver *2*, and pass dry chlorine through the system, maintaining the furnace temperature at 600-700 °C. What happens? Write the equation of the reaction.

When the chlorination process terminates, stop the heating, cool the apparatus in a chlorine stream to 300-400 °C, and displace the chlorine from the apparatus with carbon dioxide. Disconnect the receiver and rapidly close it with a weighed stopper. Weigh the receiver with the vanadium oxychloride and calculate the yield in per cent.

Remove the stopper from receiver *2* and introduce copper shavings. Close the flask with a stopper provided with a dephlegmator and thermometer (see Fig. 20). Wrap the flask in asbestos and put it into an electrical flask heater. What is the boiling point of vanadium oxychloride? Transfer the collected liquid into a weighed drawn out test tube. (*Wear eye protection, seal the substance in the presence of your instructor!*) Weigh the ampoule with the remaining part of the tube. Calculate the yield in per cent.

Hydrolysis of Vanadium Oxychloride. (*Perform the experiment in a fume cupboard!*) Pour 3-4 ml of water into a bowl and add several drops of vanadium oxychloride. What occurs?

Preparation of Vanadium Oxychloride by Reacting Vanadium(V) Oxide with Thionyl Chloride. Place 16 g of ammonium vanadate into a porcelain crucible. Roast the substance up to a constant mass at 500-550 °C in a crucible furnace, passing oxygen into the latter via a glass tube from a gas meter.

Assemble an apparatus (see Fig. 21). Place the prepared vanadium(V) oxide into a flask and add 12 ml of freshly distilled thionyl chloride. Heat the flask in a water bath for three or four hours. Replace the reflux condenser with a dephlegmator provided with an inclined cooler (see Fig. 20). Distil off the fraction boiling at 126-127 °C by carefully heating the flask with the open flame of a burner. Transfer the collected liquid into a weighed drawn out test tube. (*Wear eye protection, seal the substance in the presence of your instructor!*) Weigh the ampoule with the substance and the remaining part of the tube. Calculate the yield in per cent.

5. Preparation of Ammonium Fluovanadate(III). Assemble an apparatus as shown in Fig. 115. Put a porcelain boat with 5 g of ammonium vanadate into quartz tube *5*. Check the tightness of the

apparatus. After testing the purity of the hydrogen, switch on the furnace. Slowly raise the temperature to 500-600 °C and carry out reduction during two hours. Cool the apparatus in a stream of hydrogen. Weigh the obtained vanadium(III) oxide.

Calculate the amount of ammonium difluoride needed to prepare ammonium fluovanadate(III). Take twice as much ammonium difluoride as calculated and melt it in a copper bowl. (*Perform the experiment in a fume cupboard, wear eye protection and gloves!*)

Introduce vanadium(III) oxide into the melt while continuously stirring with a nickel spatula. Cool the melt. In an hour, grind the cooled green sinter in a porcelain mortar and again heat it in

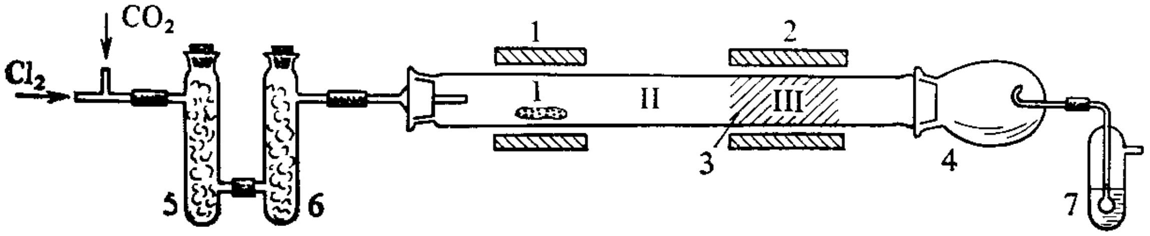


Fig. 124. Apparatus for preparing niobium (tantalum) chloride and purifying it from impurities

a platinum bowl with constant stirring. Heat until the evolution of a white smoke terminates (what is its composition?). Do not raise the temperature above 200 °C because under these conditions decomposition and oxidation of the product are possible. Write the equations of the reactions. Weigh the product and calculate the yield in per cent.

6. **Preparation of Anhydrous Dioxovanadium Nitrate (VO_2NO_3).** Prepare 7-10 ml of liquid nitrogen(IV) oxide (see p. 141). Mix the nitrogen(IV) oxide with 5-7 cm^3 of dry acetonitrile in a test tube (see Fig. 92*a*). Add 0.3-0.5 g of metallic vanadium preliminarily crushed in a porcelain mortar to this mixture. Close the test tube with a stopper provided with a calcium chloride tube containing phosphoric anhydride.

After 24 hours, distil off the excess nitrogen(II) oxide and acetonitrile on a water bath in a vacuum produced by a water-jet pump. Weigh the product and calculate its yield in per cent.

7. **Preparation of Niobium (Tantalum) Chloride and Purification from Iron Impurities.** Assemble an apparatus as shown in Fig. 124. Place activated carbon preliminarily dried in vacuum during two hours at 200-250 °C into section *III* of the reactor. Mix 2 g of niobium (tantalum) and 0.5 g of iron in a porcelain boat and place them in section *I*. Fill columns *5* and *6* with a mixture of glass wool and phosphoric anhydride, and fill wash bottle *7* with sulphuric acid.

Displace the air from the apparatus with a stream of dry carbon dioxide. Switch on furnace *1* and *2*, and raise the temperature in

them to 200 and 400 °C, respectively. Let the system stand for drying at these temperatures during 30 minutes.

Connect dry receiver *4*. Reduce the rate of flow of the carbon dioxide to one bubble a second. In 20 minutes, stop the stream of carbon dioxide and pass chlorine through the apparatus at a rate of five bubbles a second. After the entire reactor is filled with chlorine, raise the temperature in furnace *1* to 400 °C and perform chlorination during one hour. Next stop the supply of chlorine and displace it from the apparatus with dry carbon dioxide. Lower the temperature of the furnace to 350 °C and, while slowly moving furnace *1* in the direction of receiver *4*, distil off the chlorides gathered in middle section *II* through the layer of activated carbon into the receiver. Transfer the substance from receiver *4* into a preweighed weighing bottle in a dry chamber and weigh it. Calculate the yield in per cent.

Extract the activated carbon from the reactor after it cools. Wash the carbon with a 15% hydrochloric acid solution. Determine the presence of iron qualitatively in the wash water.

25 CHROMIUM, MOLYBDENUM, TUNGSTEN, URANIUM

Write the electron configurations of the chromium, molybdenum, tungsten, and uranium atoms. Why are the sizes of molybdenum and tungsten atoms almost the same? Which oxidation states are exhibited by the most stable compounds of these elements (for example, their natural compounds)? Explain the observed laws.

What place do the chromium subgroup elements occupy in the electrochemical series of the metals? How do they react with acids and with alkalies? Write the equations of the relevant reactions.

25.1 CHROMIUM

CHROMIUM(II) COMPOUNDS

Preparation of Chromium(II) Chloride. (Perform one of the following two experiments.) **1.** Put several pieces of metallic chromium into a test tube, pour in 2-3 ml of a 20% hydrochloric acid solution, and insert a stopper with a gas-discharge tube. Connect to the latter a rubber tube with a slot closed by a glass rod (a Bunsen valve, Fig. 125). What is the role of the slot in the rubber tube? Identify the substance in the solution. Write the equation of the reaction.

2. Put a few pieces of zinc into a small flask, pour in 2-3 ml of a chromium(III) chloride solution, 5-10 ml of a 10% hydrochloric

acid solution, and 0.5 ml of petrol. Close the flask with a stopper provided with a gas-discharge tube. Immerse the end of the tube into water. What is the petrol used for? How does the colour of the solution change during the experiment? Write the equation of the reaction. Keep the solution for further use.

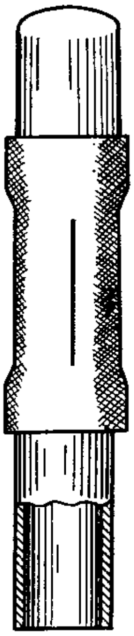


Fig. 125. Bunsen valve

Properties of Chromium(II) Chloride. Perform all experiments with chromium(II) chloride rapidly! Why?

1. Pour several millilitres of the obtained chromium(II) chloride solution into a test tube and let it stand in the air. How does the colour of the solution change? What properties are exhibited by the chromium(II) chloride? Write the equation of the reaction.

2. Put a few sodium acetate crystals into a test tube and add a chromium(II) chloride solution to them. What do you observe? Write the equation of the reaction.

3. Pour an excess of a 10% sodium hydroxide solution into a test tube with a chromium(II) chloride solution. What is obtained? What properties does chromium(II) hydroxide have?

CHROMIUM(III) COMPOUNDS

Preparation and Properties of Chromium(III) Oxide. (Perform one of the following two experiments.) 1. Take 2.5 g of comminuted potassium dichromate, mix with 0.5 g of sulphur, put the mixture into a porcelain crucible, and heat with the flame of a burner. (*Perform the experiment in a fume cupboard!*) Remove the burner when self-glowing of the mixture is noticeable. Grind the sinter in a mortar with water, filter off the chromium oxide, rinse it, and dry it in a drying cabinet. Write the equation of the reaction.

2. Spill a small amount of triturated ammonium dichromate into a small porcelain crucible and put the latter into a porcelain triangle on a ring of a stand. Spread out a sheet of paper underneath. Heat the crucible with the flame of a burner. Remove the latter as soon as the ammonium dichromate begins to decompose. Gather the chromium(III) oxide formed. Write the equation of the reaction.

How does chromium(III) oxide react with water, acid and alkali

solutions? With what reactants should chromium oxide be fused to produce sodium chromite and chromium(III) sulphate?

Preparation and Properties of Chromium(III) Hydroxide. Prepare chromium hydroxide and see how it reacts with dilute solutions of acids and alkalies. Write the equations of the reactions. What type of hydroxides does chromium hydroxide relate to? What is the structure of the hydroxochromate(III) ion?

Preparation of Chromium Potassium Alum. Pour 25 ml of water into a 50-ml beaker and dissolve 2.5 g of potassium dichromate in it. Add a concentrated sulphuric acid solution to the mixture (one-and-a-half the stoichiometric amount). First cool the mixture to room temperature, and then put it into water with ice and add ethanol dropwise from a dropping funnel until the solution acquires a violet colour (sulphur dioxide can also be used as the reducing agent). Keep the temperature below 40 °C (why?). After adding the ethanol, let the solution stand to your next lesson. Write the equation of the reaction.

Filter off the formed crystals and dry them on filter paper. Choose a well formed crystal of the alum, fasten it with the aid of a thin thread or hair to a glass rod and lower it into the mother liquor. Watch how the crystal grows several days. Examine the shape of the chromium potassium alum crystals under a microscope and compare it with that of potassium aluminium alum crystals. What will happen if crystals of potassium aluminium alum are lowered into a saturated solution of chromium potassium alum.

Define isomorphism.

Properties of Chromium(III) Salts. 1. Dissolve several crystals of a chromium(III) salt in cold water and note the colour of the solution. Heat the solution up to boiling. How does its colour change?

What structure can ions of chromium(III) have in an aqueous solution depending on the conditions? Explain the structure of aqua-complex chromium(III) ions from the viewpoint of the valence bond method.

What is the pH of a chromium(III) sulphate solution? Why?

2. Prepare a chromite solution using for this purpose the smallest possible amount of a sodium hydroxide solution, and boil it. What happens? Which salt hydrolyzes more—one of chromium(III) oxide or sodium chromite? Why? How can the hydrolysis of chromium(III) chloride be brought to the end?

3. Add an ammonium sulphide solution to one of chromium(III) sulphate. What is the composition of the precipitate? How can chromium(III) sulphide be prepared?

4. Add an excess of an alkali solution and bromine water to a chromium(III) sulphate solution. Heat the mixture. How does the colour of the solution change? Write the equation of the reaction.

CHROMIUM(VI) COMPOUNDS

Preparation of Potassium Chromate. (Perform one experiment on each table.) Melt a mixture of 1 g of potassium carbonate, 1 g of potassium hydroxide, and 2 g of potassium nitrate in an iron crucible by heating with the flame of a burner. While stirring the melt with an iron wire, introduce 1 g of finely comminuted chromite or 0.8 g of chromium oxide into the crucible. Roast the mixture for 5-10 minutes on a blowpipe. Treat the cooled melt with water. Filter the solution and evaporate it until a crystalline film appears. What is the composition of the formed crystals? Why was potassium carbonate introduced into the reaction? Write the equation of the reaction.

Properties of Chromic Acid Salts. 1. Dissolve a small amount of the prepared potassium chromate in water and add dilute sulphuric acid. What is the change in the solution's colour due to? How does the composition of chromic acid salts change depending on the reaction of the medium? Write the equations of the reactions.

2. Pour an ammonium sulphide solution into a potassium chromate or dichromate solution and heat the mixture. How does the solution's colour change? What is the composition of the precipitate? Write the equation of the reaction. What properties does chromium(VI) exhibit in this reaction? How does an acidified potassium chromate or dichromate solution react with hydrogen sulphide, sulphur dioxide, and an iron(II) salt? Write the equations of the reactions.

3. Pour potassium chromate and dichromate solutions into separate test tubes and add a solution of a barium salt to each of them. What is the composition of the precipitates? See how the obtained salts react with dilute acids. Perform similar experiments with a lead salt. Write the equations of the reactions.

Preparation of Chromic Anhydride. Place 1 g of potassium dichromate into a porcelain bowl, dissolve it in 10 ml of water, and add 6 ml of concentrated sulphuric acid while stirring with a glass rod. What substance precipitates? Cool the solution and filter off the precipitate on a funnel with a glass filtering bottom. Write the equation of the reaction.

Properties of Chromic Anhydride. (*Perform the experiment in a fume cupboard!*) 1. Put several crystals of the chromic anhydride prepared in the preceding experiment onto the lid of a crucible and pour two or three drops of ethanol onto them from a pipette. What happens? Write the equation of the reaction.

2. Dissolve part of the chromic anhydride crystals in water. Pour 2-3 ml of the solution into a test tube and add a potassium iodide solution. What is observed? Write the equation of the reaction.

Chromium Peroxide Compounds. Add a little of a dilute sulphu-

ric acid solution, 1-2 ml of ethyl ether, and a few drops of a potassium chromate or dichromate solution to 2-3 ml of a dilute hydrogen peroxide solution. Carefully stir the mixture. What is in the ether and water layers? Write the equation of the reaction.

25.2 MOLYBDENUM AND TUNGSTEN COMPOUNDS

Molybdic and Tungstic Anhydrides. Place several ammonium molybdate crystals onto the lid of a crucible and first heat them carefully, and then roast them strongly. What occurs? Perform a similar experiment with ammonium tungstate or tungstic acid. Write the equations of the reactions. At what temperature do molybdic and tungstic anhydrides sublime?

Compare the properties of the trioxides of the chromium subgroup elements (their colour, thermal stability, oxidizing ability, and reaction with water).

Molybdic and Tungstic Acids. What hydrates do molybdenum and tungsten trioxides form?

1. Pour 2-3 ml of a 10% nitric acid solution into 2-3 ml of a 20% ammonium molybdate solution. What substance precipitates? What is its colour? Wash the precipitate with water by decantation and divide it into two parts. React one part of the precipitate with an excess of concentrated hydrochloric acid and the other with a 20% sodium hydroxide solution. Explain the results. Write the equations of the reactions. Under what conditions does molybdenum(VI) oxide dihydrate form?

2. Prepare a solution of sodium tungstate containing 0.5 g of the dry salt, and pour into it an equal volume of a 10% hydrochloric acid solution. Wash the precipitate by decantation with water slightly acidified with hydrochloric acid.

What is the colour and composition of the tungsten trioxide hydrates? Test the reaction of tungstic acids with 10% solutions of alkalies and acids.

How do the stability and acid-basic properties of the hydrates of chromium, molybdenum, tungsten, and uranium trioxides change?

Salts of Molybdic and Tungstic Acids. What types of salts of molybdic and tungstic acids exist? Give examples of isopoly- and heteropoly molybdenum and tungsten compounds. What is the composition of para- and metamolybdates and of para- and metatungstates? Which molybdates and tungstates dissolve poorly in water?

Thiosalts and Sulphides of Molybdenum and Tungsten. Pour 2-3 ml of an ammonium molybdate solution into one test tube and 2-3 ml of a sodium tungstate solution into another one. Add 2-3 drops of a 25% ammonia solution to each solution and pass a stream of hydrogen sulphide through them from a Kipp gas generator. What compounds form? Acidify the solutions with a 10% hydrochloric

acid solution and slightly heat them. What is the composition of the precipitates? Write the equations of the reactions.

Reduction of Molybdenum(VI) and Tungsten(VI) Compounds. Pour 3 ml of an ammonium molybdate solution into each of four test tubes, acidify with a 2 *N* hydrochloric acid solution, and heat up to boiling. Add solutions of sulphuric acid, hydrogen sulphide, and tin(II) chloride to three of the tubes, respectively, and throw one or two small pieces of zinc into the last tube. Perform similar experiments using sodium tungstate as the initial reactant. Write the equations of the reactions.

Molybdenum and Tungsten Peroxide Compounds. Pour ammonium molybdate and sodium tungstate solutions into separate test tubes, acidify them with sulphuric acid, and add several drops of a 1% hydrogen peroxide solution to each tube. How does the colour of the solutions change? Write the equations of the reactions.

25.3 URANIUM COMPOUNDS

Uranyl Nitrate. Acquaint yourself with the appearance of uranyl nitrate. Find the solubility products of uranyl nitrate in water and ether in a reference book. What is the reaction of solutions of ammonium sulphide, potassium hexacyanoferrate(II), and potassium phosphate with a uranyl nitrate solution? What is obtained? Write the equations of the reactions.

Ammonium Diuranate. Pour 5 ml of a uranyl nitrate solution into a 50-ml beaker. Heat the solution to 80 °C and add several drops of a methyl orange solution to it. What causes the colour of the indicator to change? Carefully pour in a 10% ammonia solution containing no carbon dioxide dropwise until the colour of the indicator changes. What substance precipitates? Write the equation of the reaction.

Shake the precipitate in its mother liquor and pour the suspension into two test tubes. Add several drops of a 10% hydrochloric acid solution to one tube and a saturated ammonium carbonate solution to the other one. Why does the precipitate dissolve? Write the equations of the reactions.

How can the formed complex compound be decomposed? What substances prevent the precipitation of ammonium diuranate?

Uranium Peroxide Hydrate. Add a 3% hydrogen peroxide solution dropwise to 5 ml of a 10% uranyl nitrate solution up to complete precipitation. Filter off the product on a small filter, wash it with water, and dry it in a drying cabinet at 70 °C. What is the composition of the product? Test the reaction of uranium peroxide hydrate with 10% solutions of acids and alkalies in the cold and when heated.

Uranium Oxides. Weigh 0.5 g of uranium peroxide hydrate in a crucible and heat it in a crucible furnace with constant stirring,

keeping the temperature below 300 °C. What changes occur when uranium peroxide hydrate is heated? Which uranium oxide forms?

Divide the preparation obtained into three parts. Boil one portion in a test tube with water (how does the colour of the precipitate change?), add a dilute acid solution to the second tube, and roast the third one in a crucible at 800 °C. What substances are obtained? See how the substance formed after roasting reacts with a concentrated nitric acid solution. Write the equations of the reactions.

What other uranium oxide is known? How is it prepared?

Uranium Compounds with Lower Oxidation States. Pour 5 ml of a uranyl nitrate solution into a test tube, add 1 ml of a 10% hydrochloric acid solution, and drop one or two small pieces of zinc into the tube. How can the change in the solution's colour be explained? Pour the solution into three test tubes. Pour a potassium permanganate solution dropwise into one tube. What happens? What properties do uranium(IV) compounds have?

Add a 10% alkali solution to the second tube. What do you observe? Add a potassium fluoride solution to the third tube. What is the composition of the separated compound? Write the equations of the reactions.

SUPPLEMENTARY EXPERIMENTS AND SYNTHESES

(Hand in all the obtained preparations to your instructor.)

1. **Preparation of Chromium.** (*Perform the experiment in the presence of your instructor, in a fume cupboard! Wear eye protection or a mask!*) Roast chromium(III) oxide in an iron crucible. Triturate potassium dichromate crystals in a mortar, melt the powder in a porcelain crucible with the flame of a gas burner, pour the substance onto a glazed tile plate, and after it solidifies again triturate it into a powder. Weigh 12 g of roasted chromium(III) oxide, 12 g of the fused potassium dichromate, and 10 g of an aluminium powder, and thoroughly mix all the substances in a mortar. Spill 10 g of a calcium fluoride powder onto the bottom of a chamotte crucible, and then the prepared mixture. (If there is no chamotte crucible in your laboratory, make a box from asbestos paper in the form of a crucible and fasten it with wire.) Tamp the substance with a pestle and make a hollow in the middle using a test tube (see Fig. 120).

Prepare an incendiary mixture by shaking 5 g of an aluminium powder and 15 g of barium peroxide in a jar. (*Do not triturate the mixture in a mortar!*) Spill the incendiary mixture into the hollow made in the reaction mass and insert a magnesium ribbon cleaned of oxide. Place the crucible on a pan and spill dry sand over it from all sides. Ignite the magnesium ribbon with a burning splinter insert-

ed into a long (0.5-0.8 m) glass tube, and then step away from the crucible.

When the reaction ends, let the crucible cool, break it, extract the chromium bead, and weigh it. Determine the yield in per cent. Explain the course of the reaction.

2. Properties of Chromium. Crush the chromium bead into small pieces in an iron mortar. Note the colour of the metal in a fresh fracture, and test its hardness. To do this, scratch a glass plate with a piece of chromium. How does a magnet act on chromium?

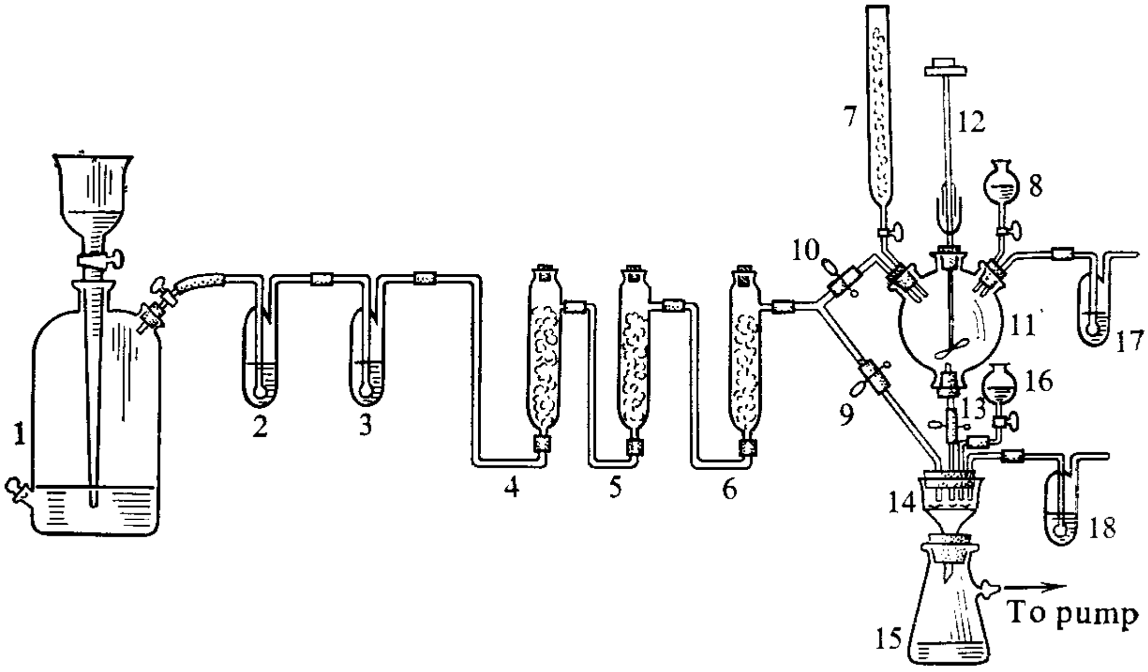


Fig. 126. Apparatus for preparing chromium(II) acetate

Put several pieces of chromium into test tubes and test its reaction with water, alkalies, and also with dilute and with concentrated solutions of hydrochloric, sulphuric, and nitric acids (in the cold and with heating). Write the equations of the reactions. What position does chromium occupy in the electrochemical series of metals?

3. Preparation of Chromium(II) Acetate. Assemble an apparatus as shown in Fig. 126. Fill wash bottles *2* and *3* with an alkaline solution of pyrogallol, and columns *4*, *5*, and *6* with solid granulated sodium hydroxide.

Prepare amalgamated zinc. To do this, place 100 g of granulated zinc into a wide-neck bottle and pour over it a solution of 0.1 *M* mercury(II) chloride in a 1 *N* hydrochloric acid solution. Close the bottle with a stopper and shake the mixture for 10-15 minutes, after which wash the amalgamated zinc first with a large amount of distilled water, and then with a 1 *N* sulphuric acid solution. Constant-

ly see that the zinc remains covered with the liquid. Transfer the zinc treated in this way into reducer *7* containing a glass wool wad on its bottom. Prepare a chromium(III) chloride solution by dissolving 30 g of chromium(III) chloride in 50 ml of dilute sulphuric acid (30 ml of water and 20 ml of 2 *N* sulphuric acid) and pour it over the zinc.

Fill dropping funnel *8* with a solution of 75 g of sodium acetate in 100 ml of water. Fill the apparatus with dry nitrogen from gas meter *1*, opening clamps *9* and *10* and closing the clamp on the rubber tube connecting flask *15* to a water-jet pump. Make sure that the nitrogen passes through wash bottles *17* and *18* filled with vaseline oil.

After the colour of the solution in reducer *7* has changed from green to bright light blue (1.5 to 2 hours), close clamp *9*, leaving clamp *10* open. Simultaneously add solutions of chromium(II) chloride and sodium acetate to vessel *11* from reducer *7* and dropping funnel *8*, switching on mechanical mixer *12*.

When precipitation terminates, close clamp *10*, open clamps *9* and *13*, and transfer the contents of vessel *11* into Büchner funnel *14* (with a filtering bottom). Switch on the water-jet pump and produce a small vacuum in flask *15*. Rinse the precipitate on the filter several times with ethanol, feeding it from dropping funnel *16*, and three times with ethyl ether. When rinsing the product the last time, disconnect the system from the water-jet pump, remove the stopper from the Büchner funnel, and thoroughly mix the precipitate with ether using a glass rod. Next suck off the ether by again connecting the system to the pump, transfer the precipitate to filter paper, and dry it in the air.

Transfer the dry chromium(II) acetate into a drawn out test tube and seal it (*wear eye protection!*). Weigh the ampoule with the substance and the remaining part of the tube, and calculate the yield in per cent.

4. Preparation of Chromium(III) Chloride Hydrate. Dissolve chromium hydroxide in concentrated hydrochloric acid, taking 35 ml of the acid for every 10 g of chromium(III) oxide contained in the hydrate. Write the equation of the reaction. Filter the solution, evaporate it on a water bath up to a syrupy consistence, pour it into a beaker, and, cooling with ice, saturate with dry hydrogen chloride. The tube supplying the hydrogen cloride should terminate in an expanding part in the form of a funnel immersed only up to 1-2 mm into the solution. Continue saturation until the solution becomes viscous owing to the precipitated crystals. Let the mixture stand in a refrigerator for 24 hours to complete crystallization. Filter off the formed crystals on a Büchner funnel without washing and dry them at 30-40 °C. What is the composition of the crystals? Describe their appearance. Calculate the yield in per cent. Store the product in a jar with a ground-glass stopper.

5. **Preparation of Anhydrous Chromium(III) Chloride.** (*Perform the experiment in a fume cupboard!*) Grind 5 g of charcoal into a fine powder in a mortar, mix it with 12.5 g of chromium(III) oxide, add a thick starch size or a dextrin solution in cold water, and make beads about 5 mm in diameter from the mixture. Put the beads onto a clay dish and dry them in a drying cabinet at 110-120 °C. Next put them into an iron crucible, cover them with the charcoal powder and a lid, and roast them.

Assemble an apparatus (see Fig. 61). Place the dry beads into a porcelain or quartz tube and perform chlorination at 750-800 °C during one hour. Chromium(III) chloride can sublime, therefore see that the tube outlet is not clogged by the product. Cool the apparatus in a stream of chlorine. Extract the beads from the tube and mechanically separate the chromium chloride formed on their surface from the unreacted charcoal. In what other ways can anhydrous chromium(III) chloride be obtained?

Put several chromium(III) chloride crystals into a test tube with water. Does the salt dissolve? Add a little of a solution of a chromium(II) or iron(II) salt. What do you observe?

6. **Preparation of Chromium(III) Nitride.** (*Work in a fume cupboard!*) Assemble an apparatus for preparing nitrides (see Fig. 84). Put 0.5-1 g of anhydrous chromium(III) chloride into a boat. Put the latter into a tubular furnace. Displace the air from the apparatus with a stream of dry ammonia and then heat the furnace to 600 °C. Continue the heating in an ammonia stream for one hour, next switch off the furnace and cool the apparatus without stopping the stream of gas. Extract the boat and weigh the product. Write the equation of the reaction. Calculate the yield in per cent.

Test how chromium nitride reacts with water and with an alkali solution in the cold and with heating. Roast part of the nitride in a porcelain crucible on the flame of a burner. Identify the product.

7. **Preparation of Chromium(III) Sulphide.** (*Work in a fume cupboard!*) Assemble an apparatus (see Fig. 115, replace the burner with a tubular furnace, pour distilled water into wash bottle *1*, and replace wash bottle *2* with a column containing phosphorus(V) oxide). Take a Kipp gas generator charged for producing hydrogen sulphide. Put 0.5-1 g of anhydrous chromium(III) chloride into a boat. Displace the air from the apparatus with a stream of dry hydrogen sulphide (how can you make sure that this has been done?) and heat the furnace to 400-500 °C. Absorb the excess hydrogen sulphide with a copper sulphate solution. Heat at this temperature for one hour, next switch off the furnace and cool the apparatus in a stream of hydrogen sulphide. Write the equation of the reaction. Weigh the product. Calculate the yield in per cent.

Put a part of the chromium sulphide into a test tube, pour in water,

and heat it. What gas evolves? How does the colour of the preparation change?

8. **Preparation of Potassium Trioxalatochromate(III).** Dissolve 3 g of potassium oxalate and 7 g of oxalic acid in 100 ml of water. Add 2.5 g of potassium dichromate to the solution in small portions with strong agitation. When the reaction terminates, evaporate the solution until almost dry and let it stand for crystallization. Filter off the precipitated crystals and examine them in transmitted and reflected light. Write the equation of the reaction.

9. **Preparation and Properties of Chromyl Chloride.** *a.* Put a mixture of 1 g of sodium chloride with 1 g of potassium dichromate into a dry test tube, add a few drops of concentrated sulphuric acid, and close the tube with a stopper provided with a gas-discharge tube. Lower the other end of the latter into another dry test tube submerged in a beaker with cold water. Slightly heat the reaction mixture. What collects in the receiver? Write the equations of the reactions.

b. Assemble an apparatus (see Fig. 104). Put sodium chloride into the Wurtz flask, and pour 70% and concentrated sulphuric acid into the dropping funnel and wash bottles, respectively. Put a small amount of chromic anhydride into the widened part of the tube. Cool the receiver—the Wurtz test tube—with water and ice. Pour an amount of water into the beaker such that the offtake provided with a funnel does not submerge into the water. Pass a stream of dry hydrogen chloride through the apparatus. What do you observe? Write the equation of the reaction. (*Never seal chromyl chloride in an ampoule!*)

Pour two or three drops of the product into a beaker with water. What is observed? Establish what ions are present in the solution. Write the equations of the reactions. What class of chemical compounds does chromyl chloride belong to?

10. **Preparation of Potassium Chlorochromate.** Introduce 2 g of powdered potassium dichromate into 4 ml of a hot 25% hydrochloric acid solution. Slightly heat the mixture. Write the equation of the reaction. What can happen if the mixture is heated for a long time?

Filter the solution on a funnel for hot filtration and let it stand up to your next lesson. Filter off the formed crystals on a glass filter. Pay attention to the shape of the crystals and compare them with potassium dichromate crystals. Dissolve a small part of the crystals in water and establish what ions are present in the solution. What properties does potassium chlorochromate exhibit? What class of chemical compounds does it belong to?

11. **Preparation of Chromium(VI) Oxysulphate.** (*Perform the experiment in a fume cupboard!*) *a. Preparation of Chromyl Chloride.* Assemble an apparatus as shown in Fig. 127*a*. Dry 12.5 g of sodium chloride and 20 g of potassium dichromate in a drying cabinet at 100-120 °C. Rapidly mix them in a mortar and put the mixture into flask *1*. Add 22 ml of a 98% sulphuric acid solution to the reaction

mixture from dropping funnel *2*. When the reaction, which first proceeds violently, slows down, heat flask *1*. Stop heating it when the evolution of the chromyl chloride terminates. Dissolve the chromyl chloride in the receiver flask in 15 ml of sulphuryl chloride. Close the

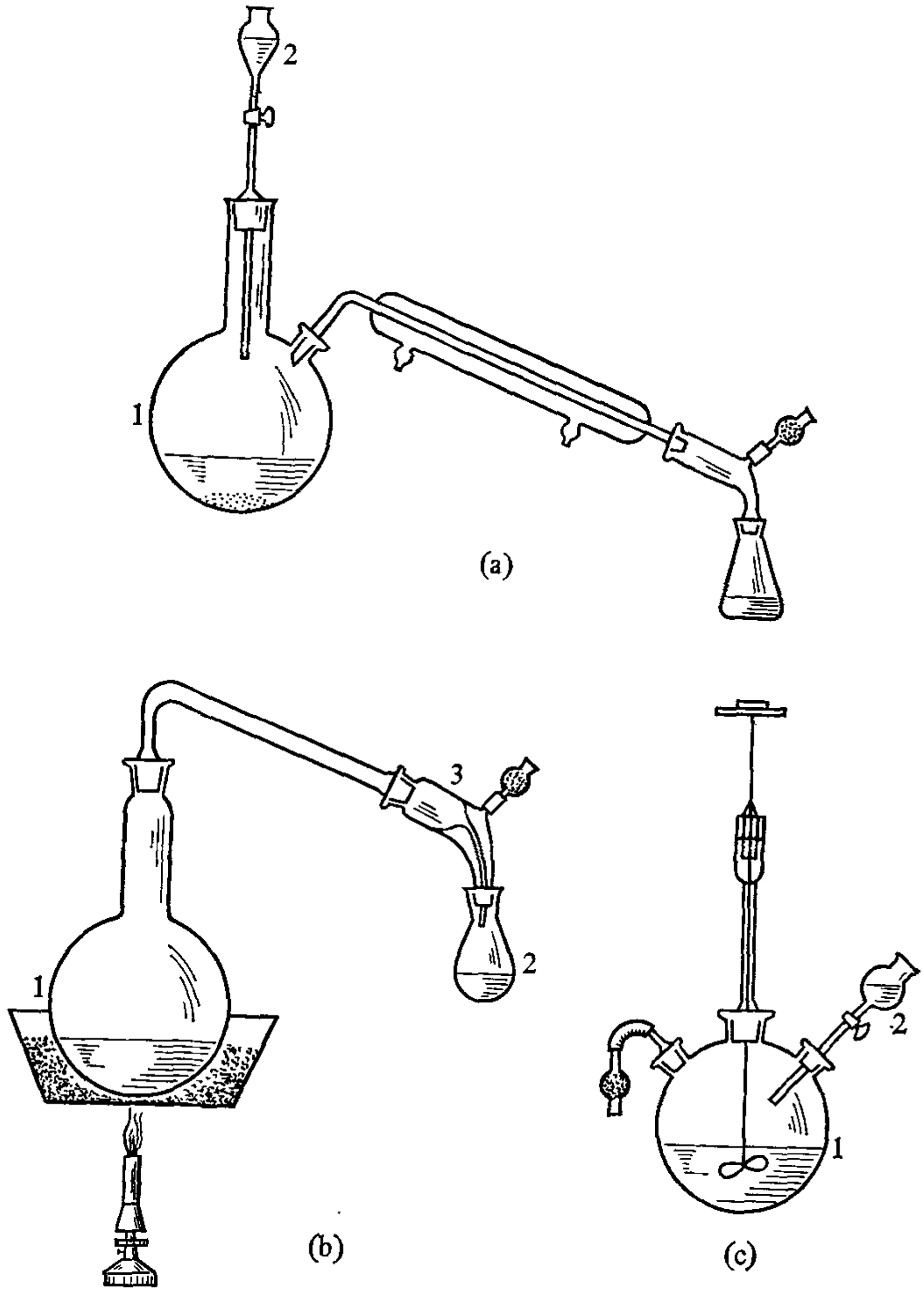


Fig. 127. Apparatus for preparing chromium(VI) oxysulphate

flask with the solution using a stopper with a ground-glass joint and keep it for the following experiment.

b. Preparation of a Sulphur Trioxide Solution in Sulphuryl Chloride. Assemble an apparatus as shown in Fig. 127*b*. Thoroughly dry all the parts of the apparatus and lubricate the ground-glass joints with concentrated sulphuric acid.

Pour 15 ml of sulphuryl chloride into flask *2* and weigh it together with its stopper. Pour 50 ml of oleum into flask *1*. Heat the latter in a sand bath and carefully distil off sulphur trioxide. Control the amount of distilled trioxide by weighing. When 12 g of sulphur trioxide are collected in flask *2*, cool the apparatus and disassemble it.

Do not wash the apparatus with water! Carefully pour out the excess oleum into a jar with a 70% sulphuric acid solution. Rinse the parts of the apparatus with a sulphuric acid solution, gradually lowering its concentration.

c. Preparation of Chromium(VI) Oxysulphate. Assemble an apparatus as shown in Fig. 127*c*. Pour a solution of chromyl chloride in sulphuryl chloride into flask *1*. Switch on the mixer and add the solution of sulphur trioxide in sulphuryl chloride to the reaction flask from funnel *2* dropwise. Filter off the precipitate in a stream of nitrogen (see Fig. 64*b*) and wash it twice on the funnel with 10-ml portions of sulphuryl chloride. Transfer the chromium(VI) oxysulphate into a weighed weighing bottle with a good ground-glass lid, weigh it, and calculate the yield in per cent.

12. Preparation and Properties of Molybdenum (Tungsten). *a.* Assemble an apparatus for preparing metals by reducing their oxides with hydrogen (see Fig. 115; replace the burner with a tubular furnace). Thoroughly check the tightness of the apparatus. Weigh about 1 g of molybdic (tungstic) anhydride in a boat and place it into a quartz tube. Check the tightness of the apparatus again. Fill the apparatus with hydrogen, check the purity of the latter, and only after this has been done switch on the furnace. Perform reduction at 800-900 °C in a stream of dry hydrogen. When the reduction process has terminated (how can this be established?), cool the apparatus in a stream of hydrogen.

b. Test the reaction of the metal with 10% and concentrated solutions of alkalies and acids in the cold and with heating.

c. Assemble an apparatus as shown in Fig. 128. Put 0.1 g of the freshly reduced molybdenum into a boat and place the latter into the reaction tube, inclining the latter in the stand as shown in the figure. Heat the flask with water up to boiling and while passing steam through the apparatus, heat the part of the tube where the boat is with a burner. Put the receiver test tube over the end of the gas-discharge tube and when it is filled with a gas, replace it with another one. Establish what gas has been collected in the test tubes. What substance has been obtained in the boat? Write the equations of the reactions.

13. Preparation of Molybdenum(VI) Oxide. *a. Preparation of Molybdenum(VI) Oxide by the Thermal Decomposition of Ammonium Molybdate.* Put a boat with 0.5 g of ammonium molybdate into a porcelain tube in an electric furnace. Connect one end of the

tube via an empty wash bottle to a water-jet pump, and the second end of the porcelain tube to a wash bottle containing vaseline oil. Switch on the water-jet pump, the electric furnace, and roast the ammonium molybdate in a stream of air first at 350-400 °C (30 min), and then at 750 °C (about an hour).

Why is the ammonium molybdate roasted in a stream of air and at two different temperatures?

Cool the apparatus in a stream of air and extract the product rom the tube. What is its appearance? Test the reaction of the

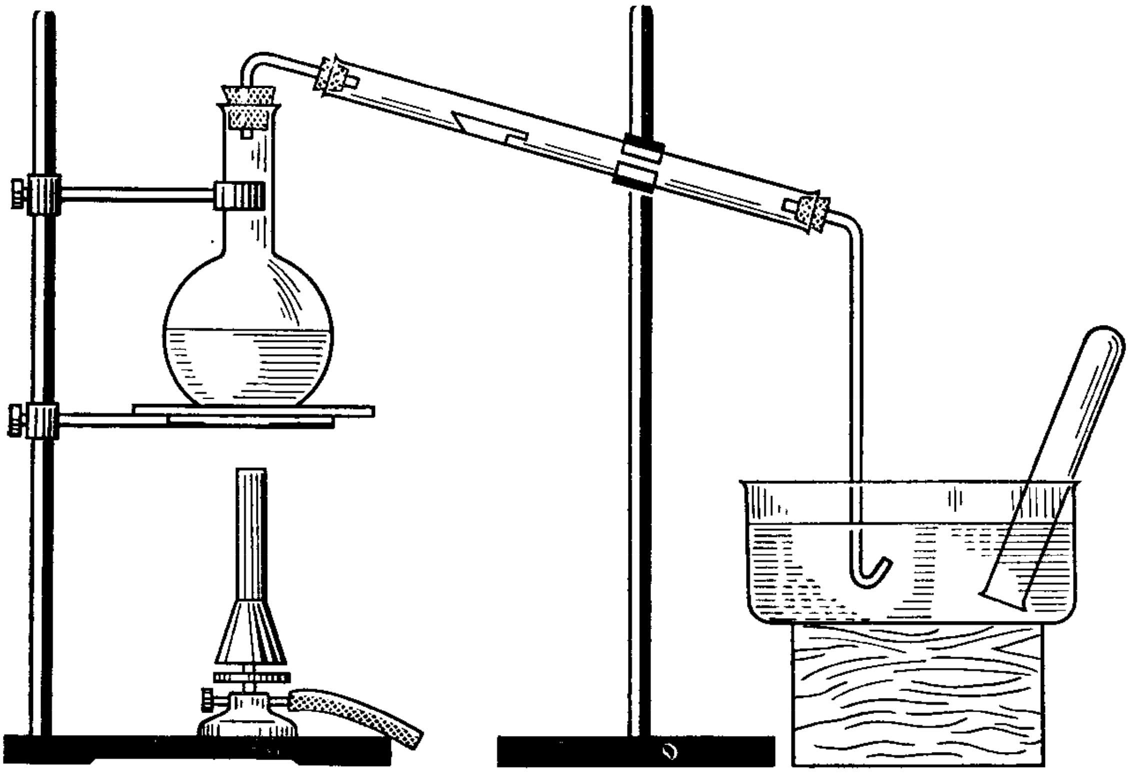


Fig. 128. Apparatus for studying the properties of metallic molybdenum

sublimed oxide with water and also with 10% solutions of hydrochloric acid and sodium hydroxide. Write the equations of all the reactions.

b. Preparation of Molybdenum (VI) Oxide by Oxidizing a Molybdenite in a Fluidized Bed. Assemble an apparatus (see Fig. 121). Put 20 g of molybdenite ground in a mortar onto porous partition *2* of quartz reactor *1*. Pass a stream of dry air via tube *3* (bottle *4* remains empty) at such a velocity that a "flame" of molybdenite appears at a distance of 30-50 mm from the edge of the horizontal bend of the reactor. Switch on furnace *5* and raise the temperature in the reactor to 600 °C.

After complete oxidation of the taken amount of molybdenite, switch off the furnace and cool the apparatus in a stream of air. Disconnect receiver *6* from the apparatus and extract the sublimed molybdenum(VI) oxide crystals from the receiver, and also from the

horizontal bend of the reactor. Weigh the substance. Calculate the yield in per cent.

14. Preparation of Sodium Paramolybdate. Pour 20 ml of a sodium molybdate solution into a 100-ml beaker. Heat the solution and introduce freshly precipitated molybdic acid into it in small portions with stirring until it stops dissolving. Filter the solution and evaporate it in a water bath until crystallization of a sample taken begins.

Examine the crystals under a microscope and compare them with crystals of the initial sodium molybdate. Cool the solution and filter off the product. What is its composition?

Pour the mother liquor into a number of test tubes and add a solution of a calcium, aluminium, or iron salt to each of them. What do you observe? Write the equations of the reactions. What is the composition of commercial ammonium molybdate?

15. Preparation of Normal Ammonium Tungstate. Weigh 0.5 g of tungstic acid in a test tube, put the latter into a cooling mixture (solid carbon dioxide with acetone), and pour in 1-2 ml of liquid ammonia. Stir the contents of the test tube with a cooled glass rod and let the ammonia evaporate. Examine the precipitated crystals under a microscope. What is the composition of the product?

16. Preparation of Sodium Paratungstate. *a.* Pour 20 ml of a 50% sodium hydroxide solution into a 100-ml porcelain beaker provided with a mechanical mixer, put the beaker on a water bath, and introduce the calculated amount of a freshly precipitated wet suspension of tungstic acid in small portions while vigorously stirring. At the end of the reaction, the pH of the solution should be 6-6.5. Filter the solution, evaporate it a little, and let it stand for 24 hours. Separate the formed crystals by filtration and dry them in the air.

b. Heat a solution of normal sodium tungstate dihydrate containing 17 g of the salt in 20 ml of water to 80 °C and add 5 N hydrochloric acid to it in small portions until the pH becomes equal to 6-6.5 (about 1.2 mol of acid per 1 mol of sodium tungstate). Heat the solution during an hour in a water bath. After filtration, let the solution stand for a day. Separate the precipitated crystals by filtration and dry them in the air. Examine the shape of the sodium paratungstate crystals under a microscope. Write the equations of the reactions.

17. Preparation of Sodium Metatungstate. Place a porous clay cylinder playing the role of a diaphragm and anode vessel into a thick-walled glass beaker (Fig. 129). Pour 300 ml of a 0.1 N sodium hydroxide solution into the glass beaker, and a solution containing 23.5 g of sodium tungstate in 100 ml of water into the inner cylinder. Lower a glass mixer into the anode compartment. A platinum plate is the anode. Use a nickel electrode in the form of a band encircling the diaphragm as the cathode.

Connect the electrolyzer to a d-c source at 6-7 V. Use rheostats R_1 and R_2 to set a current of about 5 A.

Conduct electrolysis until the pH of the solution in the anode compartment becomes equal to 3; take samples every hour. Check the completeness of converting the tungstate into the metatungstate by means of the Scheele reaction. To do this, add 1 ml of concentrated hydrochloric acid dropwise to 5 ml of a sample. The absence

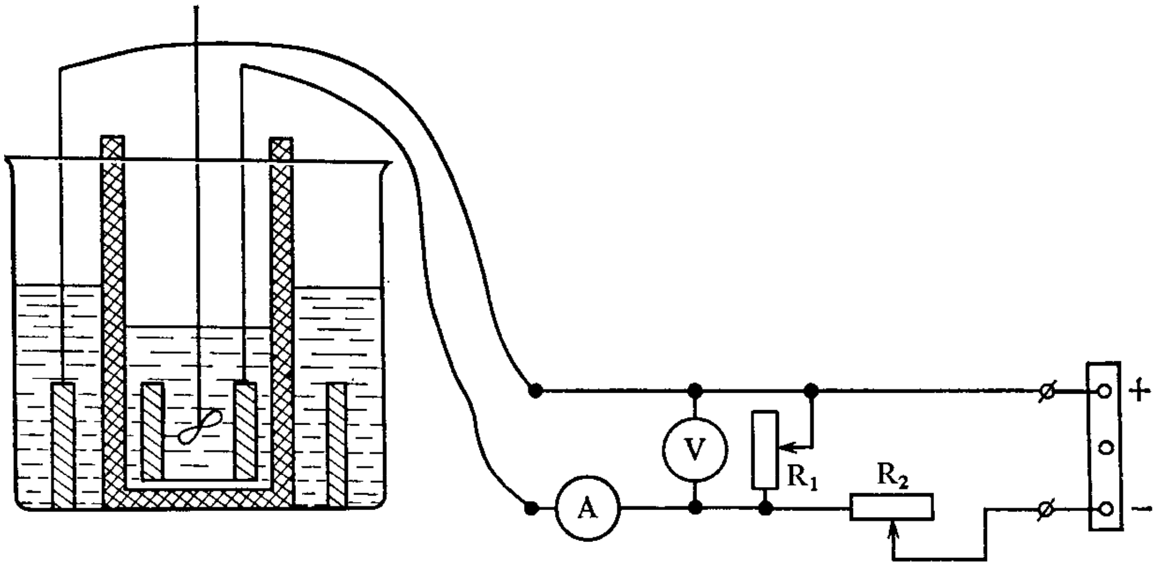


Fig. 129. Electrolyzer for preparing sodium metatungstate

of a precipitate (of what composition?) indicates that the sodium metatungstate has been converted completely.

Write the equations of the reactions occurring in the anode and cathode compartments, and also of the Scheele reaction. Transfer the anolyte and catholyte into different vessels. After the anolyte cools, check the pH of the solution again.

Evaporate the anolyte in a water bath up to one-fourth of its initial volume. Put the solution for crystallization into a desiccator over an alkali. Perform crystallization as completely as possible, but so that the mother liquor remains. Separate the crystals from the mother liquor by decantation, dry them in the air with filter paper, and weigh them. Calculate the yield in per cent.

18. Preparation of Tungsten Bronzes. Replace the burner with a tubular furnace in an apparatus for reducing metal oxides with hydrogen (see Fig. 115). Put 0.3-0.5 g of sodium ditungstate into the reaction tube in a boat. Check the tightness of the apparatus and fill it with hydrogen. Check the purity of the hydrogen and switch on the furnace. Maintain a temperature of 550 °C during one hour. Cool the reaction tube in a stream of hydrogen. What is the colour of the product?

Perform a similar experiment with sodium paratungstate, keeping the temperature within 600 °C. What properties do tungsten bronzes exhibit? Where are they employed?

19. Preparation of Potassium Hexachloromolybdate(III). (*Perform the experiment in a fume cupboard!*) Dissolve 50 g of molybdic anhydride in 250 ml of concentrated hydrochloric acid. Spill the molybdenum(VI) oxide into the beaker in small portions as it dissolves during 6 hours. If the solution is turbid, filter it through a glass filter (prepare the solution beforehand).

Transfer the solution into thick-walled glass beaker *1* containing porous clay cylinder *2* that functions as a diaphragm and anode vessel (Fig. 130). Fill the anode compartment with 12 *N* hydrochloric

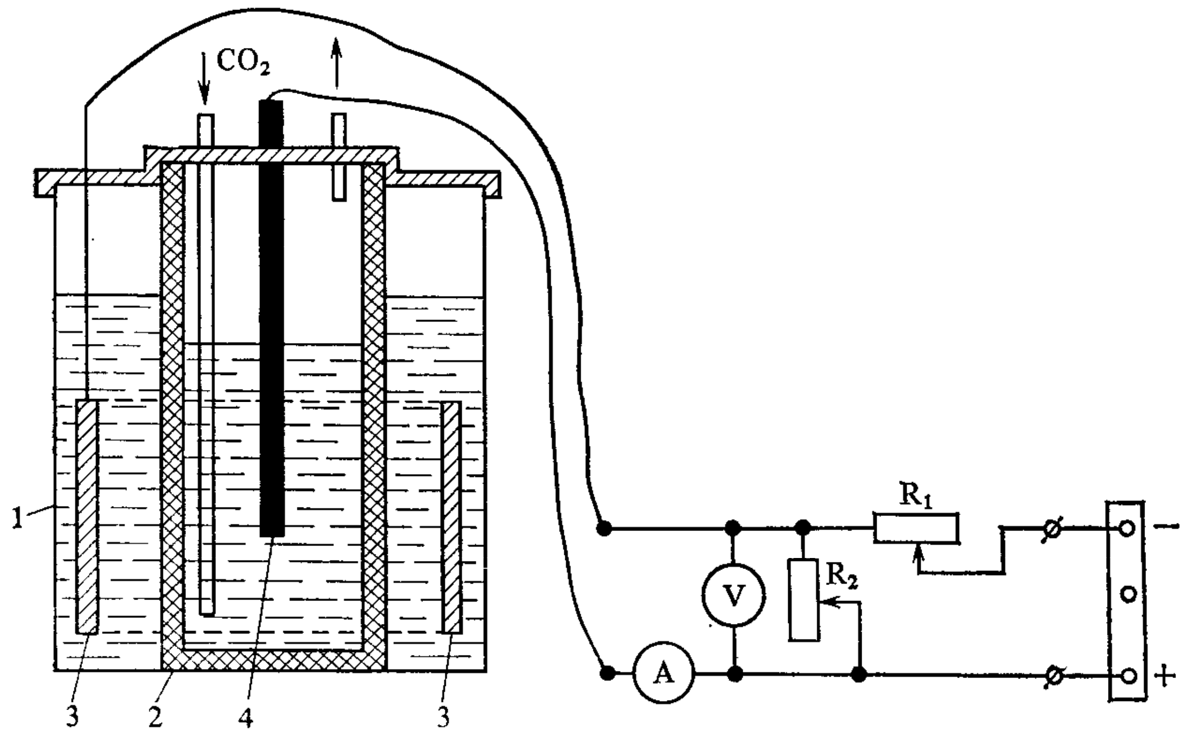


Fig. 130. Electrolyzer for preparing potassium hexachloromolybdate(III)

acid so that graphite anode *4* is submerged half way in the acid. Keep the level of the acid constant during the electrolysis. Platinum wire (or plate) *3* is the cathode. Pass carbon dioxide into the anolyte.

Connect the electrolyzer to a d-c source at about 2 V. Use rheostats R_1 and R_2 to set a current of about 5 A. The current density during the electrolysis must remain constant and be 0.07 A/cm^2. Perform the electrolysis until a sample of the solution diluted with water becomes red (in about eight hours). Write the equations of the reactions proceeding in the cathode and anode compartments.

Pour the solution obtained in reduction into a conical flask preliminarily filled with carbon dioxide and heat the reaction mixture in a stream of carbon dioxide in a water bath during an hour. Introduce 35 g of potassium chloride into the hot solution in small portions and evaporate the solution up to one-third of its volume. Close the flask with a rubber stopper and let it stand in the cold overnight.

Separate the formed crystals using a glass funnel with a filtering bottom. Wash them on the filter with absolute ethanol and dry them in a desiccator over phosphorus(V) oxide. Weigh the substance and calculate the yield in per cent.

20. Preparation of Molybdenum Pentachloride and Tungsten Hexachloride. (*Perform the experiment in a fume cupboard!*) Assemble an apparatus as shown in Fig. 131. Pour a little concentrated sulphuric acid into wash bottles *1*, *2*, and *3*. Put a layer of glass wool

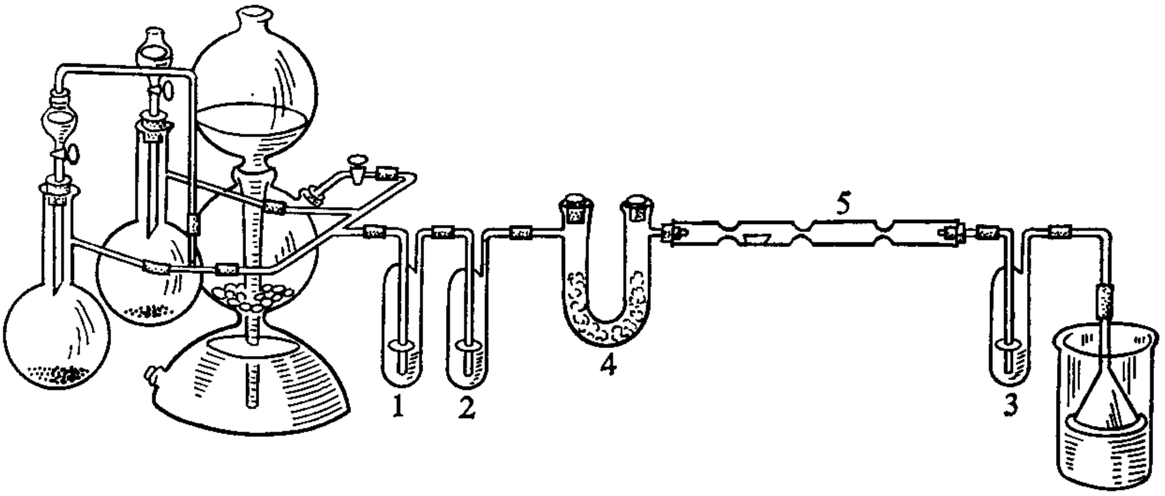


Fig. 131. Apparatus for preparing molybdenum pentachloride and tungsten hexachloride

with phosphoric anhydride into U-tube *4*. Weigh 0.5 g of the reduced molybdenum (tungsten) and put it into the first widened part of reaction tube *5*. Fill the apparatus with dry carbon dioxide. Next, while heating the place of the tube where the molybdenum is with the flame of a burner, pass a stream of dry hydrogen chloride through the apparatus. This is needed to distil off the oxychlorides formed from the oxides contained in an insignificant amount in the powdered metal. Distil off the oxychlorides to the end of the reaction tube. *Prevent clogging of the tube outlet!*

Fill the apparatus with chlorine and perform chlorination of the molybdenum, heating the place of the tube where the metal is with the flame of a burner to 200-300 °C. What colour do molybdenum pentachloride and tungsten hexachloride have? If oxychlorides are produced together with the molybdenum(V) or tungsten(VI) chlorides, distil them off in a chlorine stream. Transfer the product into a weighed test tube with a stopper, weigh it, and hand it in to your instructor. Calculate the yield in per cent.

Test the reaction of molybdenum pentachloride (tungsten hexachloride) with water. What is observed? What class of chemical compounds should the molybdenum and tungsten chlorides be related to?

21. Preparation of Molybdenum(III) Bromide. (*Perform the experiment in a fume cupboard!*) Assemble an apparatus as shown in Fig. 132 and check its tightness. Put 2-3 g of reduced molybdenum into a wide refractory Wurtz test tube. Calculate the amount of bromine needed for the bromination of the taken amount of metallic molybdenum. Pour the bromine into the dropping funnel, taking an excess of 20%.

Fill the apparatus with carbon dioxide dried by passing it consecutively through two wash bottles with sulphuric acid and a column with phosphorus(V) oxide. Raise the temperature in the furnace to 350-370 °C and, without stopping the carbon dioxide stream, add bromine dried over phosphoric anhydride dropwise at a rate such that all of it enters into the reaction. Transfer the preparation to a weighed weighing bottle and thoroughly close it. Weigh the bottle with the substance. Calculate the yield in per cent.

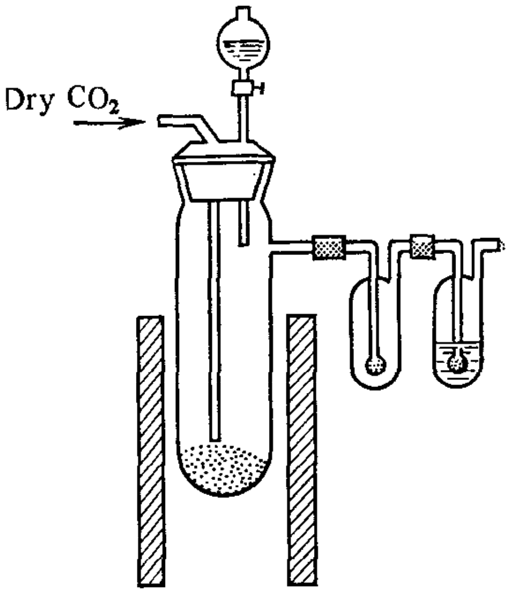


Fig. 132. Apparatus for preparing molybdenum(III) bromide

22. Preparation of Uranium(IV) Fluoride. (*Perform the experiment in a fume cupboard!*) Assemble an apparatus as shown in Fig. 133. Fill columns *2* and U-tube *4* with a mixture of glass wool and phosphoric anhydride. Put an empty graphite boat into quartz tube *3* and heat it in a nitrogen stream at 400 °C up to a constant mass. Weigh 6 g of uranium(VI) oxide in a graphite boat and place the latter into tube *3*. While passing a stream of nitrogen through the apparatus, keep the substance at 300 °C for an hour. Raise the furnace temperature to 400 °C. Stop the nitrogen stream and pass Freon-12 through the system from a cylinder via a reducer during two hours.

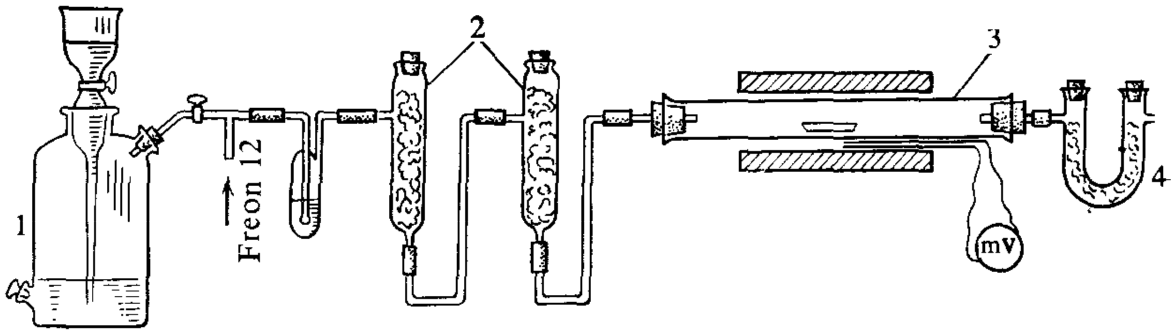


Fig. 133. Apparatus for preparing uranium tetrafluoride

Freon is the trade name for mixed methane and ethane fluorochlorides, for example, Freon-12 is CF_2Cl_2 (b.p. = — 30 °C).

Cool the apparatus in a stream of dry nitrogen. Remove the boat with the substance from the tube. After cooling it in a desiccator to room temperature, weigh in on an analytical balance. Use the change in the weight to determine whether the reaction has proceeded to the end. If it hasn't, repeat the fluorination, heating the tube for one hour. Weigh it again. Place the obtained uranium tetrafluoride in a weighing bottle and hand it in to your instructor.

23. Preparation of Uranium(IV) Chloride. (*Perform the experiment in a fume cupboard!*) *a.* Assemble an apparatus as shown in Fig. 134. To purify the hydrogen more completely from impurities,

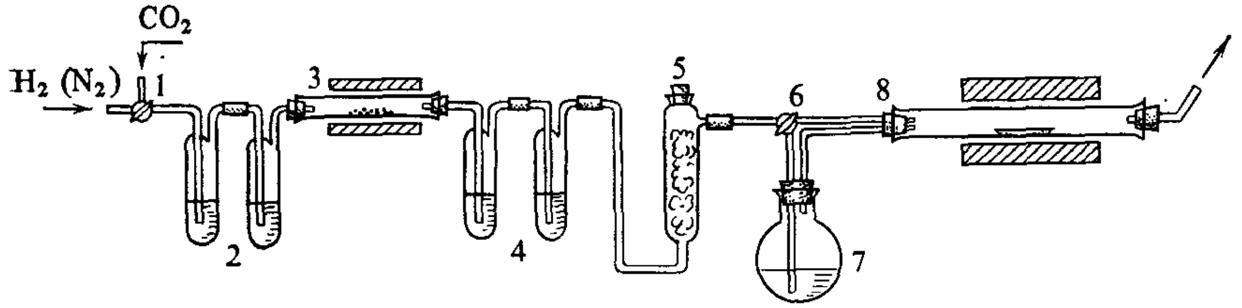


Fig. 134. Apparatus fo preparing uranium tetrachloride

pass it consecutively through wash bottles *2* with an acidified potassium permanganate solution, tube *3* with reduced copper heated by an electric furnace (600 °C), wash bottles *4* with a 96% sulphuric acid solution, and through column *5* filled with a mixture of glass wool and phosphorus(V) oxide.

Place 3 g of uranium(VI) oxide in a porcelain boat into quartz tube *8*. Check the tightness of the apparatus. Displace the air from the system with hydrogen, passing it through the cold apparatus including flask *7*. Collect the hydrogen over water and check its purity. Having made sure that the hydrogen is pure, turn cock *6* and direct the hydrogen stream into quartz tube *8*, bypassing flask *7* with carbon tetrachloride. Switch on the heating of tubes *3* and *8* and perform reduction of the uranium(VI) oxide during three hours at 500 °C.

After this, switch off the Kipp gas generator by turning cock *1* and connect a gas meter with nitrogen. Displace the hydrogen from the apparatus with nitrogen and lower the furnace temperature to 450 °C. Turn cock *6* so that a weak stream of nitrogen will entrain the carbon tetrachloride vapour (heat the flask with a water bath) when flowing into tube *8*. Perform chlorination during three hours, after which, without stopping the nitrogen flow, cool the apparatus to room temperature.

Extract the boat with the substance from the quartz tube. Transfer the preparation into a weighed weighing bottle (in a dry cham-

ber or a large desiccator filled with dry carbon dioxide). Weigh the substance and calculate the yield in per cent.

b. Active uranium(IV) oxide, which is the initial substance for preparing uranium tetrachloride, can also be obtained by decomposing uranyl oxalate trihydrate. In this case, exclude the Kipp gas generator from the apparatus. Put 5 g of uranyl oxalate trihydrate in a porcelain boat into quartz tube *8*. Displace the air from the system with a stream of nitrogen and then, without stopping the supply of nitrogen, slowly raise the temperature of the furnace to 450 °C and maintain it for two hours, after which feed carbon tetrachloride vapour into the reaction tube.

26 MANGANESE

Write the electron configuration of the manganese atom. Give examples of compounds corresponding to the different oxidation states of manganese. Indicate the position of manganese in the electrochemical series of the metals. How does it react with water, and with solutions of acids in the cold and with heating? Write the equations of the relevant reactions.

26.1 MANGANESE(II) AND MANGANESE(IV) COMPOUNDS

Manganese(II) Hydroxide. 1. Take manganese(II) chloride as the starting substance, prepare the hydroxide, study its properties, namely, its reaction with oxygen, air, acids, and alkalies.

2. Add bromine water to a small amount of the precipitate. What is formed? What properties does manganese(II) hydroxide have? Write the equations of the reactions.

Properties of Manganese(II) Salts. 1. Add an ammonium sulphide solution to a solution of a manganese(II) salt. What substance precipitates? How does the colour of the precipitate change when left in the air? Write the equations of the relevant reactions.

2. Add one drop of a silver nitrate solution and several ammonium persulphate crystals to a manganese sulphate solution acidified with sulphuric acid, and then heat the mixture. How does the colour of the solution change? What was the role of the silver nitrate? What properties do manganese(II) salts have?

Manganese(IV) Oxide. How can manganese(IV) oxide be prepared? What substances can be prepared when roasting manganese(IV) oxide depending on the temperature? What forms when manganese(IV) oxide reacts with concentrated solutions of sulphuric and hydrochloric acids? Write the equations of the reactions.

26.2 MANGANESE(VI) AND MANGANESE(VII) COMPOUNDS

Preparation of Potassium Manganate. Melt a mixture of 1 g of potassium hydroxide, 2 g of potassium carbonate, and 3 g of potassium nitrate in an iron crucible on a gas burner. While stirring the liquid mixture with an iron wire, add 1 g of powdered manganese(IV) oxide in small portions. Continue the heating while stirring until the substance becomes thick. After it cools, treat the melt in the crucible with a small amount of water. Pour off the transparent solution into a small flask and close it with a stopper; keep the substance remaining in the crucible for the following experiment. What is the colour of the solution? What substance colours it? Write the equation of the reaction.

Properties of Manganates. 1. Pour 1 ml of the prepared potassium manganate solution into each of two test tubes, greatly dilute the solution in one tube with water, add 2-3 ml of water to the other tube and pass a stream of carbon dioxide through it. How and why does the colour of the solution in both cases change? Write the equations of the relevant reactions.

2. Add a few drops of ethanol to a potassium manganate solution and carefully heat it. What happens? Write the equation of the reaction.

3. Heat 1-2 ml of an oxalic acid solution up to boiling and add a potassium manganate solution. How does the colour of the solution change? Write the equation of the reaction.

4. Pour a part of the potassium manganate solution into a small beaker and add a saturated barium chloride solution to it up to complete precipitation. What precipitates?

Properties of Permanganates. 1. Put several potassium permanganate crystals into a test tube and heat them. What gas evolves? Write the equation of the reaction.

2. Add a little alkali and a little glucose solution to several drops of a concentrated potassium permanganate solution. Heat the test tube. How does the colour of the solution change? Write the equation of the reaction.

3. Add solutions of potassium sulphide and iodide to small amounts of a potassium permanganate solution in separate test tubes. Heat the solutions. How does their colour change? What precipitates? Write the equations of the reactions.

4. Pour 0.5-1 ml of a potassium permanganate solution into each of three test tubes, acidify with sulphuric acid, and add solutions of iron(II) sulphate, hydrogen sulphide, and sulphurous acid to them, respectively. How does the solution's colour change? Write the equations of the reactions.

How does the medium affect the nature of reduction of the permanganate in an aqueous solution? Compare the values of the standard electrode potentials of the permanganate ion in an acid and neutral media (see Appendix 1, Table 21).

5. Add a potassium permanganate solution dropwise to a manganese sulphate solution in a test tube. What occurs? Write the equation of the reaction.

Preparation and Properties of Manganic Anhydride. (*Perform the experiment in a fume cupboard, in the presence of your instructor!*) **1.** Triturate several potassium permanganate crystals into a powder and spill it into a small porcelain bowl. Use a pipette or glass tube to wet the salt with a few drops of a 96% sulphuric acid solution. What forms?

2. Wet the end of a glass rod with the prepared mixture and bring it up to ethyl ether poured into a porcelain bowl. What happens?

You can light an alcohol burner with alchohol in the same way. *Never repeat the experiment using the same rod!*

Write the formulas of all the manganese oxides and compare their properties. How and why do the properties change in the series of manganese hydroxides corresponding to its different oxidation states? Which of the manganese hydroxides are unstable in air?

Which elements are analogues of manganese? Give a general characteristic of the elements of the manganese subgroup.

SUPPLEMENTARY EXPERIMENTS AND SYNTHESES

(Hand in all the obtained preparations to your instructor.)

1. **Preparation of Manganese by the Aluminothermic Process.** (*Perform the experiment in the presence of your instructor!*) Put 20 g of finely comminuted manganese(IV) oxide into a porcelain crucible and roast it in a muffle or crucible furnace at 800 °C during an hour. What forms? Why is manganese(IV) oxide not used directly for producing metallic manganese by the aluminothermic process?

Thoroughly mix the product of roasting with 5 g of aluminium shavings in a porcelain mortar. Put the mixture into a chamotte crucible surrounded with dry sand (*in a fume cupboard*!). If there is no chamotte crucible in your laboratory, make a box from asbestos paper in the form of a crucible and fasten it with wire. Add 10 g of an incendiary mixture (see p. 202) to the crucible, insert a magnesium ribbon, and ignite it with a burning splinter inserted into a long glass tube (see Fig. 120). After cooling the crucible, break it, free the metal bead of slag, weigh it, and keep it for further experiments. Calculate the yield in per cent.

Properties of Manganese. Break up the manganese bead with a pestle in a steel mortar or with a hammer. Give attention to the brittleness of the metal, note its colour in a fresh fracture, test it with a magnet, see how it reacts with water, an alkali solution, and also with dilute and concentrated solutions of hydrochloric, sulphuric, and nitric acids (in the cold and with heating). Write the equations of the reactions.

2. **Preparation of Manganese Chloride in an Ethanol Solution.** Assemble an apparatus (see Fig. 116), replacing dropping funnel *2* with a gas-supply tube. Put 3 g of small pieces of metallic manganese and 100 ml of absolute ethanol into flask *1*. Switch on the mixer. Cool the flask with dry ice and saturate the ethanol with thoroughly dried hydrogen chloride (about one or two hours). Stop the cooling and retain a weak stream of the hydrogen choride. If the reaction slows down, immerse the flask into a water bath (50-60 °C).

Separate the solution from the unreacted metal by decantation. Transfer the solution into a wide test tube (see Fig. 118). Distil off the ethanol in a vacuum produced by a water-jet pump while carefully heating the test tube in a beaker with boiling water. What crystallizes in the tube?

Perform desolvation of the manganese chloride in a vacuum produced by a water-jet pump while carefully heating the test tube with the flame of a burner. Transfer the product into a weighed weighing bottle, weigh it, and calculate the yield in per cent.

3. **Preparation of Manganese Oxalate.** Prepare 5 ml of a potassium permanganate solution saturated at 60 °C and 7.5 ml of an oxalic acid solution saturated at the same temperature. Transfer the latter solution into a flask for suction, acidify it with acetic acid, and add the potassium permanganate solution to it. What happens? Write the equations of the reactions. Close the neck of the flask with a stopper, and fit a rubber tube closed with a rod onto the offtake opening. When the precipitate coagulates, open the offtake opening, partly open the stopper, and carefully pour the liquid off the precipitate. Next add a triple amount (by volume) of distilled water to the precipitate, shake it, and again close the opening. Rinse the precipitate three times by decantation.

Filter off the rinsed precipitate on a Büchner funnel and dry it at a temperature not exceeding 100 °C. What is produced if the salt is roasted without the access of air?

4. **Preparation of Manganese(II) Oxide.** Dehydrate 1 g of manganese oxalate by heating in a porcelain bowl at not over 200 °C. Transfer the salt into a porcelain boat and roast it in a tubular furnace in a stream of dry hydrogen at 300-400 °C (see Fig. 115). Preliminarily check the tightness of the apparatus and the purity of the hydrogen!

When the hydrogen evolving from the tube contains no carbon dio-

xide (how can this be checked?), switch off the furnace and cool the preparation in a stream of hydrogen. Remove the boat from the tube, spill out its contents onto hot asbestos, and see what happens to the preparation in the air. Write the equations of the reactions.

5. **Preparation of Sodium Manganate(V).** Put 2 g of finely powdered potassium permanganate, 50 ml of a 28% sodium hydroxide solution, and 3.5 g of thoroughly triturated sodium sulphite heptahydrate into a 200-ml beaker. Place the latter in a bath with a mixture of ice and sodium chloride. Stir the reaction mixture while cooling it until it transforms into a homogeneous light-blue crystalline substance. Filter it off on a glass filter No. 3 (400 mesh). Wash the precipitate on the filter with a 28% sodium hydroxide solution cooled to 0 °C and then with a small amount (15-20 ml) of ethanol cooled to —10 °C.

Transfer the crystals into a previously weighed weighing bottle, weigh it, and calculate the yield.

Dissolve a small amount of the salt in a 50% potassium hydroxide solution. What do you observe? Write the equation of the reaction.

6. **Preparation of Sodium Manganate(VI) by the Solid-Phase Reaction of Manganese Dioxide with Sodium Peroxide.** Pour 15-

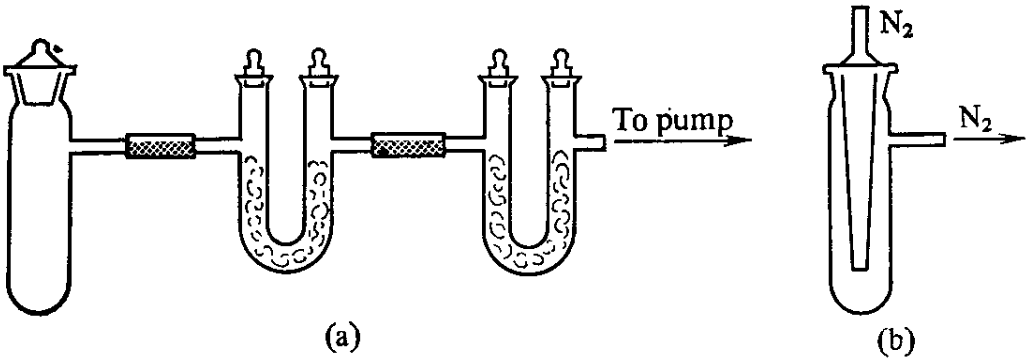


Fig 135. Apparatus for preparing sodium manganate(VI)

20 ml of dry carbon tetrachloride into a thoroughly dried weighing bottle. Put about 4 g of sodium peroxide under the carbon tetrachloride layer and weigh the bottle with an accuracy up to 0.1 g. Calculate the amount of manganese dioxide needed for complete reaction with the sodium peroxide and weigh it with the same accuracy.

Transfer both compounds into a porcelain mortar with dry carbon tetrachloride (about 20 ml). Rinse the walls of the weighing bottle that contained the sodium peroxide with a small amount of carbon tetrachloride (2-3 ml) and add this solution to the reaction mixture.

Place the mortar into a water bath (*in a fume curboard!*). When the solvent boils, thoroughly grind the mixture with the pestle of the mortar during 30 minutes. Transfer the obtained paste into a test tube with an offtake (Fig. 135*a*) and connect it via a drying system

to a water-jet pump. While heating in the water bath, pump out the carbon tetrachloride remaining in the mixture during an hour.

Disconnect the apparatus from the water-jet pump and pass nitrogen (or argon) over the reaction mixture (Fig. 135*b*) after purifying it from oxygen by passing it through wash bottles containing an alkaline solution of pyrogallol. Put the vessel into a crucible furnace. Slowly raise the temperature in the furnace to 450 °C and hold the reaction mixture under these conditions for 1.5 hours.

The reaction has proceeded to the end if a sample of the formed dark green, almost black, sodium manganate dissolves completely in water.

7. **Preparation of Potassium Permanganate by the Hydrolysis of Potassium Manganate.** Triturate the potassium manganate remaining in the crucible (see "Preparation of Potassium Manganate", p. 236) in a mortar, transfer it into a flask, add 100 ml of water, and boil it, passing a stream of carbon dioxide through the flask, until the liquid acquires a crimson colour. Let the solution settle, and then filter it through a funnel with a glass filter. What remains on the filter? Evaporate the solution in a water bath until crystallization begins and cool it. Filter off the precipitated crystals and dry them. Write the equations of the reactions. How is potassium permanganate produced in the industry?

8. **Preparation of Potassium Permanganate by the Anode Oxidation of Manganese.** Assemble an electrolyzer (see Fig. 130). Use an iron wire as the cathode and immerse it into the porous clay vessel. Take a piece of manganese produced by the aluminothermic process as the anode and fasten it in place with a thin platinum wire. Only the manganese should be submerged in the electrolyte in the anode compartment!

Pour 200 ml of a potassium carbonate solution saturated at 0 °C into the electrolyzer and connect the electrodes to a d-c source at 36 V through a rheostat and ammeter. Maintain the temperature of the bath during work at 50-60 °C. The current during electrolysis should be 1 A. Continue electrolysis for 30 minutes. How does the colour of the solution change in the anode compartment? Write the equations of the electrochemical reactions.

Weigh two samples of sodium oxalate of about 0.01 g each on an analytical balance and put them into two dry 250-ml conical flasks. Add 20 ml of a 20% sulphuric acid solution to each flask. Take two samples of the obtained potassium permanganate solution with a 10-ml pipette, transfer them into the flasks containing the sodium oxalate samples, and shake them. What happens? Titre the excess oxalic acid with a potassium permanganate solution of a known concentration. Calculate the amount of potassium permanganate formed and the yield relative to the current.

Check the properties of potassium permanganate (see above).

27 IRON, COBALT, NICKEL

Indicate the position of iron, cobalt, and nickel in Mendeleev's periodic table of the elements, the electron configurations and sizes of their atoms, and their oxidation states. Explain the observed law of the change in the characteristic oxidation states in the series iron-cobalt-nickel. Why do the elements of the iron family fail to exhibit the highest oxidation state corresponding to the number of the group in the periodic table which they belong to?

What oxidation states are exhibited by the platinum metals—analogues of the iron family elements? In what are they similar to iron, cobalt, and nickel?

27.1 PROPERTIES

What position is occupied by the iron family elements in the electrochemical series of the metals? How do they react with water, acids, and alkalies? Write the equations of the reactions of iron with dilute and concentrated hydrochloric, sulphuric, and nitric acid solutions in the cold and with heating.

How do iron, cobalt, and nickel react with the oxygen of the air? What is the rusting of iron? What factors affect this process? What will happen if we take two plates, one of galvanized iron and the other of tin-plated iron, scratch each of them with a file to remove the protective layer of metal, wet them with a 10% sodium chloride solution, and let them stay in the air?

27.2 COMPOUNDS

PREPARATION AND PROPERTIES OF HYDROXIDES

Iron(II) Hydroxide. Prepare 200 ml of water containing no dissolved oxygen. To do this, boil distilled water for 5-10 minutes while passing carbon dioxide through it, and then cool the water in a stream of carbon dioxide to room temperature. Close the mouth of the flask with a stopper.

Using this water, dissolve several crystals of Mohr's salt (what is its composition?) in a test tube, acidify the solution with sulphuric acid, and put a few pieces of iron into it (for what purpose?). Prepare a sodium hydroxide solution in another test tube. By adding the alkali solution to that of the Mohr's salt, prepare a precipitate of iron(II) hydroxide. What is its colour? What happens to it in the air? Write the equations of the reactions.

Perform a similar experiment, using iron(II) sulphate and alkali solutions at hand in the laboratory. Compare and explain the results obtained.

Iron(III) Hydroxide. Prepare iron(III) hydroxide and study its reaction with an acid and an excess of an alkali. Write the equations of the reactions.

Which of the hydroxides—iron(II) or iron(III)—has stronger basic properties and how can this be explained?

Cobalt(II) Hydroxide. Add a small amount of a sodium hydroxide solution to one of a cobalt(II) salt. Note the colour of the precipitate formed. Add some more alkali and heat the mixture, shaking the contents of the test tube. How does the colour of the precipitate change? What happens to the cobalt(II) hydroxide when it stands in the air? Write the equations of the reactions.

Cobalt(III) Hydroxide. Pour a cobalt(II) salt solution into two test tubes, add bromine water to one of them, hydrogen peroxide to the other, and then pour a sodium hydroxide solution into both tubes. What happens? Write the equations of the reactions.

Nickel(II) Hydroxide. Prepare nickel(II) hydroxide. Does it change when left in the air? Write the equations of the reactions.

Nickel(III) Hydroxide. Add bromine water to a precipitate of nickel(II) hydroxide. What happens? Write the equation of the reaction. How can you explain the different reaction of iron(II), cobalt(II), and nickel(II) hydroxides with the oxygen of the air? Why does the method of preparing cobalt(III) and nickel(III) hydroxides differ from that of preparing iron(III) hydroxide? How and why do the acid and basic properties of iron, cobalt, and nickel hydroxides change depending on their oxidation state?

SALTS

Preparation of Mohr's Salt. (*Perform the experiment in a fume cupboard!*) Put one gramme of a finely cut iron wire into a flask and dissolve it with heating in the calculated amount of 2 *N* sulphuric acid. Insert a funnel into the neck of the flask (for what purpose?). Keep the volume of the solution constant. After dissolving the metal, filter the solution and evaporate it until a crystalline film begins to form on its surface. What substance is in the solution?

Prepare with heating a saturated ammonium sulphate solution in an amount such that there is one molecule of this salt per iron atom. Mix the prepared hot solutions and let them crystallize. Filter off the crystals on a Büchner funnel, wash them with a small amount of cold water, and dry them on filter paper. Weigh the salt and calculate the yield in per cent.

Dissolve several crystals of the salt in water and determine what ions are present in the solution. What class of compounds does this

salt belong to? Put the salt into a small jar with a well fitting stopper. Write the equations of the reactions.

Properties of Iron(II) Salts. 1. Test a solution of Mohr's salt with an indicator. Write the equation of the iron(II) sulphate hydrolysis reaction. Pour in a sodium carbonate solution. What do you observe? Write the equation of the reaction and explain the results obtained.

2. Pour a potassium hexacyanoferrate(III) (potassium ferricyanide) solution into a Mohr's salt one. What is obtained? Write the equation of the reaction. What is this reaction used for?

3. Add a potassium permanganate solution to one of an iron(II) salt acidified with sulphuric acid. What happens? Write the equations of the reactions of an iron(II) salt with potassium permanganate and with potassium dichromate. Will an iron(II) salt be oxidized by chlorine, bromine, and iodine water (see Appendix 1, Table 21)? How do iron(II) salts react with hydrogen sulphide and ammonium sulphide?

What conclusions on the properties of iron(II) salts can be made from the above experiments? Why should freshly prepared Mohr's salt be used as the starting substance when studying the properties of iron(II) compounds?

Properties of Iron(III) Salts. 1. Determine the pH of an iron(III) chloride solution. Write the equation of the hydrolysis reaction of this salt. Which salt—iron(II) sulphate or iron(III) sulphate—hydrolyzes more strongly in solutions?

2. Add a sodium carbonate solution to one of iron(III) chloride. What is the composition of the precipitate? Write the equation of the reaction.

3. Pour 1-2 ml of an iron(III) chloride solution into each of two test tubes. Add several drops of an ammonium thiocyanate solution to one of the tubes, and a potassium hexacyanoferrate(II) (potassium ferrocyanide) solution to the other one. What happens? Write the equations of the reactions. What are these reactions used for?

4. How does iron(III) chloride react with sodium sulphide and potassium iodide? Write the equations of the reactions. Under what conditions do iron(III) salts transform into iron(II) ones and vice versa?

5. What happens when iron(III) chloride reacts with hydrogen sulphide and ammonium sulphide? Conduct the relevant reactions and write their equations. List the properties of iron(III) salts. How can sodium ferrite be prepared? Which salts hydrolyze more strongly—ferrites or iron(III) salts? What does this depend on?

Preparation and Properties of Ferrates. Put about 0.5 g of triturated potassium hydroxide (if possible, containing no carbonate) into a porcelain bowl, add 3-5 drops of an iron(III) chloride solution and 3-5 drops of bromine (*in a fume cupboard!*). After heating

for a short time in a water bath, cool the bowl with its contents, add 15-20 ml of water, and transfer the solution into a small beaker. What substance colours the solution?

Pour the ferrate solution into three test tubes. Add a barium chloride solution to one tube up to complete precipitation. What is the composition of the precipitate? Pour hydrogen sulphide water into the second tube, and 2 *N* sulphuric acid into the third one. What is observed? Write the equations of all the reactions. What properties do iron(VI) compounds have?

Properties of Cobalt(II) Salts. 1. Put several crystals of anhydrous cobalt(II) chloride into a test tube and wet them with water. How does the colour change? Add concentrated hydrochloric acid. What is the solution's colour now?

2. Pour 1-2 ml of absolute ethanol into a test tube and add a few cobalt(II) chloride crystals. Explain the change in colour.

3. Pour a cobalt(II) sulphate solution into two test tubes. Add hydrogen sulphide water to one of them, and a sodium sulphide solution to the other. What do you observe?

Properties of Cobalt(III) Compounds. Roast a few cobalt(II) nitrate crystals in the flame of a gas burner. How can you determine the end of the reaction?

Put a small amount of the obtained cobalt(III) oxide (what other cobalt oxide can form depending on the temperature?) into a test tube and treat it with concentrated hydrochloric acid. What gas evolves? Write the equations of the reactions. How does cobalt(III) oxide react with nitric and sulphuric acids? Write the equations of the reactions.

Properties of Nickel(II) Salts. Test the reaction of hydrogen sulphide and sodium sulphide with a solution of a nickel(II) salt. Acquaint yourself with the values of the solubility products of nickel and cobalt sulphides.

Why is the formation of simple (not complex) salts not characteristic of cobalt(III) and especially of nickel(III)?

27.3 COMPLEX COMPOUNDS

COMPOUNDS WITH COMPLEX CATIONS

Cobalt and Nickel Ammines. First add a little, and then an excess of a concentrated ammonia solution to solutions of cobalt(II) and nickel(II) salts. What do you observe? Boil the ammonium solution of the cobalt salt while shaking the test tube (for what purpose?). Explain the changes in its colour. Write the equations of the reactions.

What is the coordination number of cobalt and nickel in the ammines? What type of complexes (strong-field or weak-field) do they belong to? What type of orbital hybridization occurs in the formation of these complexes? What spatial configuration does this correspond to?

How does the stability of ammines change in the series iron(II), cobalt(II), nickel(II)?

COMPOUNDS WITH COMPLEX ANIONS

Potassium Hexanitrocobaltate(III). Add a little acetic acid and an excess of potassium nitrite to a cobalt(II) salt solution. Heat the mixture. What gas evolves? What precipitates? Write the equation of the reaction. What is the coordination number of cobalt in this compound?

What is the composition of iron, cobalt, and nickel carbonyls? Consider the structure of the carbonyls of these elements from the standpoint of the valence bond theory.

SUPPLEMENTARY EXPERIMENTS AND SYNTHESES

(Hand in all obtained preparations to your instructor.)

1. Preparation of Reduced Iron (Cobalt, Nickel). (*Wear eye protection or a protective mask!*) Assemble an apparatus for reducing metal oxides with hydrogen (see Fig. 115; replace the burner with a tubular furnace). Charge the Kipp gas generator to produce hydrogen. Consecutively fill wash bottle *1* with an alkaline solution of lead acetate, *2* with an acidified solution of potassium permanganate, and connect two more wash bottles with concentrated sulphuric acid (for what purpose?). Pour water into the crystallizer. Check the tightness of the apparatus.

Weigh about 0.5 g of iron oxide in a porcelain boat and place the latter into a tube for roasting in an inclined tubular furnace. Insert a thermocouple into the furnace and connect it to a pyrometer. Why must the furnace be inclined somewhat?

Again check the tightness of the apparatus and the purity of the hydrogen. Switch on the furnace and roast the iron oxide in a stream of hydrogen at 600-650 °C during an hour. How can the end of the process be determined?

Switch off the furnace and cool the apparatus in a hydrogen stream to room temperature. Extract the boat and put the iron into a jar with a well fitting ground-glass stopper. Test the initial iron oxide and the reduced iron with a magnet. How does iron react with acids and alkalies?

2. Preparation of Pyrophoric Iron. Thoroughly triturate iron(III) oxide in an agate mortar and roast it in a hydrogen stream at 400-500 °C (see the preceding experiment). Cool the furnace to 100 °C, extract the boat, and spill the iron powder into a heated porcelain bowl. What happens?

3. Preparation of Iron(II) Oxide. *a*. First prepare iron(II) oxalate. To do this, pour an ammonium oxalate solution into 20 ml of a Mohr's salt solution up to the complete precipitation of the iron. Wash the precipitate several times with water by decantation, next filter it on a Büchner funnel, wash off sulphate ions, and dry it at 100 °C.

b. To prepare iron(II) oxide, assemble an apparatus (see Fig. 115) (*perform the experiment in a fume cupboard!*). Displace the air from the apparatus with carbon dioxide. Roast 2 g of the iron(II) oxalate in a quartz tube in a carbon dioxide stream at 500-600 °C.

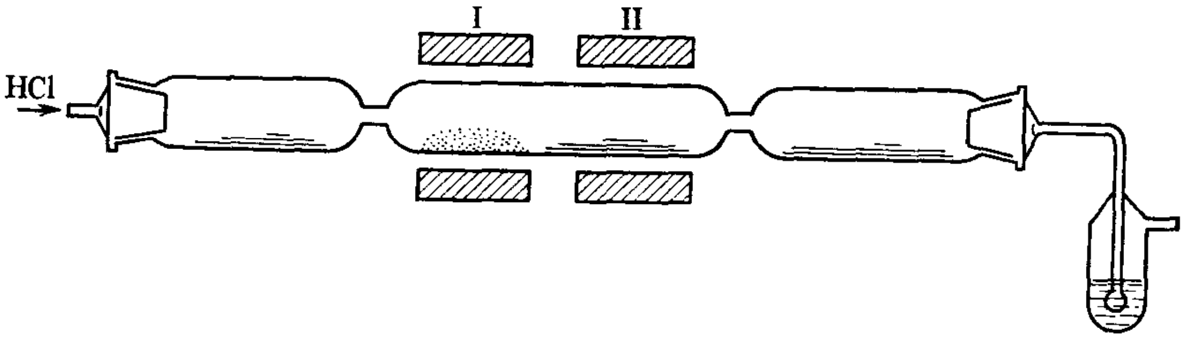


Fig. 136. Quartz tube for preparing macrocrystalline iron(III) oxide

When the reaction terminates, cool the apparatus in a stream of carbon dioxide and rapidly spill the product into a small jar preliminarily weighed and filled with carbon dioxide. Close the jar with its stopper and weigh it. Calculate the yield in per cent. What is the colour of the iron(II) oxide? What is obtained when iron(II) oxide is roasted in the air? When storing a jar with iron(II) oxide, pour paraffin over it.

4. Preparation of Macrocrystalline Iron(III) Oxide. Assemble an apparatus for preparing hydrogen chloride. To dry the gas well, install a column with phosphorus(V) oxide in addition to two wash bottles with sulphuric acid. Spill amorphous iron(III) oxide into the middle part of a three-section quartz tube (Fig. 136). Put the latter into a two-zone furnace. To retain the temperature difference, wrap the unheated zone (the middle of the tube) with asbestos.

Pass a slow stream of thoroughly dried hydrogen chloride through the tube at a rate of one or two bubbles in three seconds during four hours. Gradually raise the temperature in the first zone to 1000 °C, and in the second zone to 800 °C. Do this during two hours, retain the maximum temperature in the furnace for half an hour, and

begin slow cooling. When heating and cooling the furnace, maintain a constant temperature difference of about 200 °C between the heating zones.

5. **Preparation of Nickel(III) Oxide.** Pour a little of a sodium hydroxide solution into a small amount of a nickel sulphate one while stirring, and then add a chlorinated lime (calcium hypochlorite) solution (which must be absolutely transparent). Let the mixture stand for several hours until the evolution of oxygen bubbles stops. Next heat it up to boiling. Let the mixture settle and wash the precipitate by decantation. Write the equation of the reaction.

Put a small amount of a nickel oxide into a test tube and treat it with concentrated hydrochloric acid. What substances separate when nickel oxide is reacted with hydrochloric, nitric, and sulphuric acids? Write the equations of the reactions. What properties does nickel oxide have?

6. **Preparation and Properties of Sodium Ferrite.** Mix 2 g of an iron(III) oxide powder and 20 g of anhydrous sodium carbonate in an iron crucible. Fuse the mixture on the flame of a gas burner or in a muffle furnace at 800-900 °C. Pour out the hot melt onto a glazed tile. When it solidifies, grind pieces of the melt in a mortar and spill the powder into a beaker with water. What settles onto the bottom of the beaker? Write the equations of the reactions. What type of oxides does iron(III) oxide belong to? Which salts hydrolyze more strongly, iron(II) or iron(III) salts? What does this depend on?

7. **Preparation of Anhydrous Cobalt (Nickel) Chloride in an Ethanol Solution.** For the procedure of running the experiment, see supplementary experiment 2 on p. 238.

8. **Preparation of Anhydrous Iron(III) Chloride in a Fluidized Bed.** For the procedure of running the experiment, see supplementary experiment 5 on p. 203.

9. **Preparation of Potassium Trioxalatoferrate(III).** First prepare barium oxalate. To do this, add a solution of 2.5 g of barium chloride dihydrate in 6 ml of water to a solution of 1.5 g of sodium oxalate in 40 ml of water. Filter off the formed crystals on a Büchner funnel and wash them several times with cold water.

To prepare potassium trioxalatoferrate(III), put 1.25 g of iron(III) sulphate, the prepared barium oxalate, 1.5 g of potassium oxalate, and 30 ml of water into a 500-ml beaker. Heat the mixture for several hours in a water bath, maintaining a constant volume. After separation of the barium sulphate precipitate, evaporate the filtrate to a volume of 5 ml and cool it. Filter off the potassium trioxalatoferrate(III) crystals, rinse them with a small amount of water and then with ethanol, and dry them in a vacuum-desiccator over sulphuric acid. Write the equations of the reactions.

Protect the preparation from sunlight. It is prudent to dry it in a dark place. How can you prove that the preparation is a complex

compound? Place a part of the potassium trioxalatoferrate(III) crystals on a watch glass and put it in sunlight. What happens to the salt?

10. Preparation of Tetraamminecarbonatocobalt(III) Nitrate. Add 10 ml of a 25% ammonia solution to a solution containing 4 g of ammonium carbonate in 20 ml of water and transfer the mixture into a 100-ml quartz flask. Add a second solution containing 6 g of cobalt nitrate hexahydrate in 12 ml of water to the first solution. Close the Wurtz flask with a stopper containing a tube reaching up to the bottom, connect the flask to a water-jet pump, and blow air through it during an hour. For what purpose is the air blown through the flask?

Pour the solution into a bowl, filter it if required, and evaporate it in a water bath, gradually adding 2 g of ammonium carbonate until crystallization begins. If the solution contains a precipitate, filter it off and leave the bowl with the solution in the bath, stopping its heating. Examine the crystals under a microscope.

Filter off the crystals on a Büchner funnel, wash them with a small amount of ice-cold water, then with dilute ethanol, and, finally, with a 96% ethanol solution. Write the equations of the reactions. Dry the salt in the air and weigh it. Calculate the yield in per cent. Prove that you have obtained a complex cobalt salt.

11. Preparation of Ammonium Hexafluocobaltate(II). *Preparation of a Cobalt(II) Chloride Solution.* Assemble an apparatus (see Fig. 116), replacing dropping funnel *2* with a gas-discharge tube. Put 1.5 g of powdered metallic cobalt and 50 ml of absolute ethanol into the three-neck flask. While vigorously agitating the flask contents with the mechanical mixer, pass a strong stream of thoroughly purified hydrogen chloride through the flask. Saturate the solution with hydrogen chloride during an hour while cooling the reaction flask with dry ice. Stop the cooling and retain a weak stream of hydrogen chloride. If the reaction slows down, immerse the flask into a water bath at 50-60 °C. Decant the solution obtained from the unreacted metal.

Preparation of Ammonium Hexafluocobaltate(II). Dissolve 1.5 g of ammonium fluoride in 100 ml of methanol. Why should methanol be taken? Filter the solution. While stirring the ammonium fluoride solution, add to it a cobalt(II) chloride solution up to complete precipitation. Separate the product with the aid of a glass filter No. 2 (270 mesh) and wash it with ether (why is this washing necessary?). Dry the product in the air, weigh it, and calculate its yield in per cent.

12. Preparation of Hexaamminenickel(II) Chloride. Dissolve 25 g of nickel nitrate in the smallest possible amount of water and add an amount of a 25% ammonia solution such that the initially formed precipitate would completely dissolve. If the initial salt was insuf-

ficiently pure, iron, aluminium, manganese, and lead hydroxides may remain in a precipitate. Filter the solution. Add an ammonium chloride solution saturated at 25-30 °C and a 2 *N* ammonia solution up to complete precipitation of hexaamminenickel(II) chloride. Immediately filter off the precipitate on a Büchner funnel and wash it twice with a solution of the precipitant, next with a concentrated ammonia solution, a mixture of ethanol and a concentrated ammonia solution (1:1), and, finally, with a pure 96% ethanol solution. Dry the product at a temperature not over 100 °C. Prove that the product is a complex compound.

13. Preparation of Nickel Carbonyl. (*Perform the experiment in the presence of your instructor! Work in a fume cupboard! Nickel carbonyl is extremely poisonous!*)

Assemble an apparatus as shown in Fig. 137. Fill the gas meter with pure carbon monoxide and charge a Kipp gas generator for

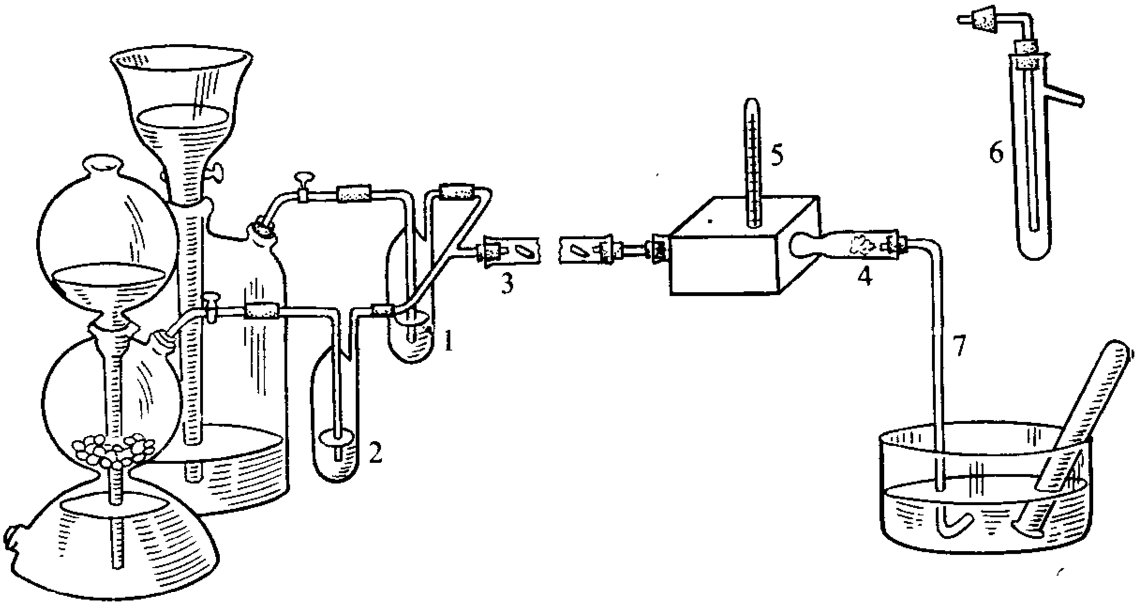


Fig. 137. Apparatus for preparing nickel carbonyl

producing hydrogen. Pour a concentrated alkali into wash bottle *1* connected to the gas meter, and concentrated sulphuric acid into bottle *2* connected to the Kipp gas generator. Put copper foil rolled up into a spiral (for what purpose?) into refractory tube *3*. Introduce glass wool mixed with 3-5 g of finely ground nickel oxalate into the front part of reaction tube *4* with a drawn out part. Fill the tube along its length over 8-10 cm. Move heating asbestos sleeve *5* onto this place of the tube. The thermometer inserted into the sleeve must reach the surface of the tube. Remove the particles of the salt from the shorter part of the tube after the constriction. Fit flame spreaders onto the gas burners. Arrange the reaction tube with a slight inclination.

Disconnect receiver test tube *6* and connect gas-discharge tube *7* instead of it. Displace the air from the apparatus with carbon monoxide. Check the purity of the evolving monoxide by collecting it from tube *7* into a test tube and lighting it. Stop the supply of the carbon monoxide and pass a strong stream of hydrogen through the apparatus. Thoroughly check the purity of the hydrogen at the outlet of tube *7* and light it. Heat the copper foil to a red heat. After this, carefully heat the nickel oxalate layer, never raising the temperature above 200 °C (at a high temperature the dispersion of the reduced nickel diminishes, which consequently lowers its activity).

When the reaction mixture becomes black, remove the condensed water from the outlet of the tube by careful heating. Let the tube cool to 70 °C in a slowed up stream of hydrogen. Remove gas-discharge tube *7* and connect receiver test tube *6*. Stop the supply of hydrogen and pass a slow stream of carbon monoxide through the apparatus (the copper foil should be red hot), maintaining the temperature within 70-80 °C. Give attention to the brightness of the flame. Introduce a cold porcelain bowl into the middle of the flame. What is deposited on it?

Slightly heat the reaction tube near the constriction and to its right. What do you observe in the part of the tube that is after the constriction? When 0.5-1 ml of the liquid product gathers in the receiver test tube, stop the supply of the carbon monoxide and cool the apparatus in a hydrogen stream. *When disassembling the apparatus, do not inhale the gases!* What was collected in the receiver test tube? Write the equations of the reactions.

28 COPPER, SILVER, GOLD

Write the electron configurations and the sizes of the atoms of the copper subgroup elements. What oxidation states do these elements exhibit in their compounds? Give examples. What position do they occupy in the electrochemical series? Write the equations of the reactions of copper, silver, and gold with acids. Give a comparative general characteristic of the physical and chemical properties of the elements of Group one.

28.1 COPPER

Preparation of Copper from Copper Sulphate by Displacement by Metallic Zinc. Prepare 5 ml of a copper sulphate solution saturated in the cold, pour it into a porcelain bowl, and introduce the calculated amount of zinc dust into it in small portions. Put the

bowl with the reaction mixture on a water bath and heat it to 80 °C. When dissolving of the zinc terminates, pour off the solution, treat the separated copper precipitate with a 5% hydrochloric acid solution, wash it with water by decantation, transfer it onto a filter, rinse it again with water, and dry it between sheets of filter paper. Store the metal in a tightly closed jar. Why? Put a small amount of the copper into an open beaker or onto a watch glass and let it stand to your next lesson. What happens to the copper when it stands in the air? Write the equations of the reactions. How is copper produced in the industry?

COPPER(I) COMPOUNDS

Preparation of Copper(I) Oxide. Dissolve 2.5 g of copper vitriol (copper sulphate pentahydrate) in 15 ml of warm water and add 1.5 g of glucose. Heat the solution and rapidly add 2.5 ml of a 20% sodium hydroxide solution to it. Stir the mixture and let it stand for an hour. Wash the precipitate with distilled water. Write the equations of the reactions.

Properties of Copper(I) Oxide. Test the reaction of the copper(I) oxide obtained with solutions of acids and ammonia. To do this, place the copper(I) oxide into four test tubes. Treat the substance in the first tube with concentrated sulphuric acid while heating it. Watch what happens. What is obtained in the solution and in the precipitate?

Add concentrated hydrochloric acid dropwise to the second tube until the appearing white precipitate dissolves. What is its composition? Explain the dissolving of the precipitate in an excess of this acid. Keep the solution for the following experiment.

Dissolve the copper(I) oxide in the third and fourth tubes in a 25% ammonia solution. Rapidly close one of them tightly with a stopper, leave the other one open, and vigorously shake both tubes. Does the colour of the solution change? Explain what you observe. Write the equations of the reactions.

Consider the structure of the copper(I) ammine complex from the viewpoint of the valence bond theory.

Preparation and Properties of Copper(I) Hydroxide. Add a 20% sodium hydroxide solution slowly, dropwise, to a hydrochloric acid solution of copper(I) oxide (see the preceding experiment). What do you observe? What is the composition and colour of the precipitate? Pour the solution off the precipitate and add to the latter (dropwise) 1-2 ml of a 10% ammonia solution. What happens? Explain the dissolving of the precipitate.

Copper(I) Chloride. 1. Dissolve 1 g of copper(II) chloride in 12 ml of water. Add 2 ml of concentrated hydrochloric acid to the solution and introduce 1.5 g of copper in the form of small pieces of thin

wire or shavings. Heat the reaction mixture (adding water to keep the volume of the solution constant) until a sample of the solution introduced into a test tube with pure water stops colouring the latter light blue. When the reaction terminates, pour tbe solution into a beaker with 50 ml of cold water. What is observed?

Filter off the precipitated copper(I) chloride, wash it first with water, and then two or three times with ethanol. See how the salt reacts with hot concentrated hydrochloric acid and a 25% solution of ammonia. Let the hydrochloric acid solution and ammonia solution stand in the air. What do you observe?

2. Put a small amount of the copper(I) chloride crystals on a watch glass and leave them in the air. What do you observe? Introduce a part of the crystals into a test tube containing 2-3 ml of a saturated sodium or potassium chloride solution. When the crystals dissolve, add 1-2 ml of water to the tube. Explain the observed phenomena. Write the equations of the reactions. Retain the remaining salt.

Copper(I) Bromide. Prepare 10 ml of a 20% aqueous solution of copper(II) bromide, heat it, and pass into it a stream of sulphur dioxide. What substance precipitates? Filter off the crystals, wash them with water, and dry them in a vacuum desiccator over potassium hydroxide.

Spill a small amount of the copper(I) bromide into three test tubes and test its reaction with water, concentrated hydrochloric acid, and ammonia, respectively. Write the equations of the reactions.

Copper(I) Iodide. Pour together equal volumes of 1 *N* copper sulphate and potassium iodide solutions. What is observed? Pass a stream of sulphur dioxide through the mixture. How does tbe colour of the solution change? Write the equations of the reactions.

Filter off the product and wash it with water. Put a small amount of the copper iodide into three test tubes. Pour an ammonia solution into one of them, concentrated hydrochloric acid into the second, and carefully heat the third tube on a gas burner. How can you explain the change in the colour of the copper(I) iodide when it is heated? How can the instability of copper(II) iodide be explained?

COPPER(II) COMPOUNDS

Preparation of Copper(II) Oxide. Add a hot copper sulphate solution to a small amount of a hot 5% sodium hydroxide solution up to the complete precipitation of the copper(II) oxide. Heat the reaction mixture while stirring during 10-15 minutes. What is observed?

How does copper(II) oxide react with dilute and concentrated nitric, hydrochloric, and sulphuric acids, and also with sodium hydroxide in the cold and with heating? Write the equations of the reactions.

Preparation and Properties of Copper(II) Hydroxide. 1. Add 0.5 ml of glycerin to a copper sulphate solution to prevent dehydration of

the copper(II) hydroxide. While stirring the solution, slowly add a 2% sodium hydroxide solution up to complete precipitation of the copper(II) hydroxide. Wash the precipitate by decantation with cold distilled water containing 1 ml of glycerin per litre of water up to removal of the sulphate ions, filter it on a Büchner funnel, and rinse it once more with water.

2. Put the copper(II) hydroxide into a number of test tubes and see how it reacts with a solution of 1 *N* hydrochloric acid, a 30% sodium hydroxide solution, and an excess of a 25% ammonia solution.

Heat one sample of the copper(II) hydroxide. Explain the observed phenomena. Write the equations of the reactions. What properties does copper(II) hydroxide have? In the form of what ion is copper present in an ammonia solution?

Preparation of a Complex Ammonium Salt of Copper(II). Dissolve 0.5 g of finely triturated copper(II) sulphate pentahydrate in 12.5 ml of a 15% ammonia solution. If the solution is turbid, filter it. Slowly add 7.5 ml of ethanol to the filtrate and let it stand for a few hours in the cold. Filter off the formed crystals, wash them first with a mixture of ethanol and a concentrated ammonia solution (1:1), and then with ethanol and ether. Dry them at room temperature. Into what ions does the product dissociate in the solution? Consider the structure of the complex ion from the viewpoint of the valence bond theory.

Dissolve several crystals of the obtained salt in a small amount of water. Pour the solution into two test tubes, add 1-2 ml of a sodium hydroxide solution to one of them and hydrogen sulphide water to the other. What is observed? How can you explain the different reaction of the sodium hydroxide solution and hydrogen sulphide with the solution of the obtained salt?

Preparation of Copper(II) and Ammonium Sulphate. Dissolve 1 g of copper(II) sulphate pentahydrate in 2 ml of water with heating and prepare a solution containing an equimolecular amount of ammonium sulphate saturated at 60 °C. Pour together the two hot solutions, mix them, and let them stand for crystallization. Examine the crystals under a microscope and compare their shape with that of copper(II) sulphate pentahydrate and ammonium sulphate crystals. What is the composition of the product? Into what ions does this salt dissociate in an aqueous solution? Check whether copper(II) hydroxide will precipitate from an aqueous solution of the obtained salt when a sodium hydroxide solution is added to it?

28.2 SILVER

The experiments are demonstrated and explained by two students. After work, the remaining silver preparations and their solutions are to be handed in to the laboratory assistant.

PROPERTIES

1. Establish in what acids and under what conditions silver can be dissolved.

2. Pour 2-3 ml of hydrogen sulphide water into a test tube and immerse a silver wire into it. What happens? Why do silver articles turn black in the air? Find the value of the solubility product of silver sulphide (see Appendix 1, Table 12).

3. Immerse a copper plate or wire cleaned with emery paper into a 0.01 *N* solution of silver nitrate. What is observed? What place does silver occupy in the electrochemical series of the metals?

COMPOUNDS

Oxides. *Silver(I) Oxide.* Introduce 1 ml of a 0.1 *N* silver nitrate solution into a test tube, and add 1 ml of a 0.1 *N* sodium hydroxide solution. Wash the precipitate with water by decantation and dry it in the air. What is the composition of the compound?

Put a small amount of the compound into a test tube and test how it is affected by heating. Treat the remaining silver compound with a 25% ammonia solution. What happens? Write the equations of the reactions.

Silver(II) Oxide. Add a soda solution and a potassium persulphate solution to 1 ml of a 0.1 *N* silver nitrate solution. What is the composition of the precipitate? Write the equation of the reaction. What physical method can be used to distinguish silver(I) oxide from silver(II) oxide?

Silver(I) Salts. Which silver salts dissolve well in water?

Silver Nitrate. Dissolve several silver nitrate crystals in water and determine the pH of the solution. Does silver nitrate hydrolyze? Is silver hydroxide a strong or a weak base? What products are obtained in the thermal decomposition of silver nitrate? Write the equation of the reaction.

Silver Halides. Taking silver nitrate as a reactant, prepare silver chloride, bromide, and iodide, Wash the precipitates with water by decantation and test the action of light, an ammonia solution, and a sodium thiosulphate solution on them. Explain the observed phenomena. Write the equations of the reactions. Explain why silver iodide dissolves in sodium thiosulphate and does not dissolve in an aqueous solution of ammonia.

How can you explain the change in the colour of the silver halides with an increase in the atomic number of the halogen? Compare the solubility products of silver halides and sulphide (see Appendix 1, Table 12). What anion is the most sensitive reagent for the silver ion? What is the significance of silver halides in photography? What substances are used in developing photographs?

SILVER PLATING

Preparation of an Ammonia Solution of Silver. Dissolve 0.25 g of silver nitrate in 4 ml of water, and carefully, dropwise, add a concentrated ammonia solution until the precipitate dissolves (what is its composition?). Add 9 ml of a 3% sodium hydroxide solution, and then more ammonia solution until the turbidity vanishes. Pour the solution into a measuring cylinder and add water up to a volume of 20 ml. Store the reagent in the dark. Why?

Preparation of a Glucose Solution. Dissolve 0.4 g of glucose in 8 ml of water, add one drop of a concentrated nitric acid solution, and boil the mixture during two minutes. Cool the solution and add an equal volume of ethanol (for what purpose?).

Cleaning of a Test Tube before Silver Plating. Thoroughly wash a test tube with a hot solution of a chromium mixture (see the first footnote on p.22), tap water, distilled water, and, finally, ethanol.

Coating the Test Tube Walls with Silver. Mix the ammonia solution of silver with the glucose solution in the proportion 10:1. Pour 4-5 ml of the reaction mixture into the prepared test tube and lower the latter into a beaker with warm water (50-60 °C). What do you observe? Write the equations of the reactions. How can the walls of the tube be cleaned of the deposited silver?

28.3 GOLD

(All the experiments are demonstrated by the instructor.)

PROPERTIES

Dissolution of Gold Foil. Put a small piece (about 0.01 g) of gold foil into a small porcelain bowl, treat it with 3-5 drops of aqua regia, and evaporate on a water bath. What forms? Leave a part of the product dry, dissolve the remainder in the smallest possible amount of water, and use the solution for the following experiments.

Colloidal Solution of Gold (Red Gold Hydrosol). Pour 5 ml of distilled water and 0.3 ml of a 0.5% gold chloride solution neutralized with soda into a wide test tube. Heat the reaction mixture until it boils, next stop the heating, add in small portions 3 ml of a 96% solution of ethanol and resume heating up to the appearance of a cherry red colour of the solution. When the latter cools, pour in 0.3 ml of a 20% hydrochloric acid solution. What do you observe? Does the sol coagulate?

Cyanide Method of Dissolving Gold. Put 0.01 g of gold foil into a test tube, add the calculated amount of a 0.03% sodium cyanide solution (*in a fume cupboard!*), and, while shaking the contents of

the tube, slightly heat the reaction mixture. What occurs? Write the equation of the reaction.

What techniques are used to extract gold from rock?

COMPOUNDS

Gold(III) Hydroxide. Pour 1 ml of a prepared solution of gold(III) chloride into a test tube and carefully neutralize it with a 0.01 *N* alkali solution. What precipitates? Pour off the solution, divide the precipitate into two parts, treat one part with concentrated hydrochloric acid and the other with an alkali. What properties does the product have? Write the equations of the reactions.

Hydrochloro-Auric Acid. Treat gold with aqua regia. When the metal dissolves, add 1 ml of concentrated hydrochloric acid and evaporate the solution until crystals appear. What is the composition of the obtained substance? Dissolve several crystals of the compound in water, add to one half of the solution several drops of a soluble cesium salt, and to the other half a 0.1 *N* potassium hydroxide solution. What forms? Write the equations of the reactions.

SUPPLEMENTARY EXPERIMENTS AND SYNTHESES

1. Preparation of Copper(II) Fluoride. *Work with hydrofluoric acid in a fume cupboard in rubber gloves, using platinum or lead ware.*

To measure a definite volume of hydrofluoric acid, you can use an ordinary clean and dry glass measuring cylinder whose inner walls have been coated with a thin layer of paraffin. How does hydrofluoric acid react with glass?

Put 0.5 g of copper(II) oxide into a platinum bowl and add the calculated amount of an approximately 35% hydrogen fluoride solution, taking an excess of 10-15%. If the reaction proceeds very slowly, put the bowl on a hot water bath. Filter the solution, inserting the filter into a lead, copper, or platinum funnel, and evaporate it until crystallization begins. Filter off the precipitate and wash it twice with cooled distilled water. Determine the yield in per cent.

2. Preparation of Copper(II) Nitride. Assemble an apparatus (see Fig. 84). Use an electrical furnace to heat reaction tube *8*. Put 2 g of copper(II) fluoride into porcelain boat *7* and place the latter into the reaction tube of the apparatus. Pass a stream of dry ammonia through the apparatus. Switch on furnace *6* and in half an hour the furnace used to heat tube *8*, heating the latter to 280 °C. Why should not the temperature be increased above 300 °C? When the reaction terminates (how can you determine this?), cool the apparatus in an ammonia stream. Put a small part of the product into a test tube and

heat it. Comment on your observations. Write the equation of the reaction.

3. Preparation of Copper(II) Bromide. Introduce 1-2 g of a copper powder into a beaker with 50 ml of water and while stirring the reaction mixture, slowly add 3-6 drops of bromine from a dropping funnel. When the reaction terminates, cool the solution, filter it through ordinary cotton wool inserted into a glass funnel, boil it with charcoal (for what purpose?), and evaporate it in a vacuum desiccator. Filter off the formed crystals on a funnel with a filtering bottom. What is the composition of the product? Write the equation of the reaction. Test how the copper bromide crystals behave in water and when heated. To do this, put 5-6 small crystals of the salt into each of two test tubes. Carefully add water dropwise to one of the tubes until the solution acquires a light blue colour, and then introduce about 0.2 g of dry potassium bromide, and heat the second tube. What happens? Explain the observed phenomena.

4. Preparation of Copper(II) Acetylide. *Perform all experiments with copper acetylide very carefully in a fume cupboard with its glass window lowered, wear eye protection! Dry copper acetylide ignites spontaneously!*

Assemble an apparatus for preparing acetylene (see Fig. 54). Put about 5 g of calcium carbide into 25-ml round-bottomed flask *1*. Fill dropping funnel *2* and cylinder *3* with a 25% sodium chloride solution. Pour a little of a 1-2% sodium hydroxide solution into wash bottle *4*, and a 2% potassium dichromate solution acidified with a dilute sulphuric acid solution into test tube *5*. By adding the sodium chloride solution in small portions to the calcium carbide, achieve a uniform stream of gas. When the apparatus is filled with pure acetylene, test the gas for the absence of air in it. How can this be done?

Put 1 g of copper(I) chloride into a beaker and add to it a 25% ammonia solution up to complete dissolution of the salt from a dropping funnel secured over the beaker. Pass a stream of acetylene through the prepared solution. What substance is formed? When the precipitation terminates, displace the acetylene from the apparatus with nitrogen.

Filter off the substance obtained in the beaker, wash it with water, ethanol, and ether, dry it in the air, and place small portions of it into several test tubes.

Spill out one portion of the copper acetylide onto an asbestos gauze and slightly heat it, apply a drop of bromine with a rod to another sample, and introduce a third sample into a test tube filled with chlorine. Wet the remaining substance with concentrated hydrochloric acid. Explain the observed phenomena.

5. Preparation of Silver from Silver Chloride. Put 1 g of silver chloride and 1.8 ml of a 40% formalin solution into a porcelain beaker and add a 30% sodium hydroxide solution in small portions

with vigorous stirring. Wash the separated silver with a dilute sulphuric acid solution, an ammonia solution, again with water, dry it between sheets of filter paper, and hand it in to the laboratory assistant. Write the equations of the reactions.

29 ZINC, CADMIUM, MERCURY

Write the electron configurations of the atoms of the zinc subgroup elements. What oxidation states do these elements exhibit in their compounds? Give examples. What position do these elements occupy in the electrochemical series?

Give a general characteristic of the elements of Group two of Mendeleev's periodic table of the elements. Underline the similarity and difference in their properties, in particular their ability to form complex compounds.

29.1 ZINC AND CADMIUM COMPOUNDS

Oxides. Put several zinc and cadmium nitrate crystals onto the lid of a crucible, heat them first carefully, and then roast them strongly. What do you observe? What is the colour of the obtained oxides? Write the equations of the reactions.

Hydroxides. Add a small amount of a 1 *N* sodium hydroxide solution to solutions of zinc and cadmium salts, respectively, and then add an excess of the hydroxide. What is observed? Write the equations of the reactions. What properties of zinc and cadmium hydroxides are characterized by these reactions?

Perform a similar experiment with zinc and cadmium salts, using an aqueous ammonia solution instead of the sodium hydroxide. Why do zinc and cadmium hydroxides dissolve in an excess of ammonia? Write the equations of the reactions. Under what conditions does the complete precipitation of zinc and cadmium hydroxides occur?

Sulphides. Acquaint yourself with the solubility products of zinc and cadmium sulphides (see Appendix 1, Table 12). Prepare the sulphides of these metals from solutions of zinc and cadmium nitrates. What should be used as the precipitant—hydrogen sulphide or ammonium sulphide? Note the colour of the precipitates and test their reaction with 1 *N* solutions of sulphuric and hydrochloric acids.

29.2 MERCURY

When working with mercury and its compounds, observe the following rules:

1. Always place all apparatuses and ware containing mercury on a special enamelled tray made from iron and having high sides.

2. Perform experiments with mercury in a fume cupboard on a similar tray.

3. Pour all residues of mercury and solutions containing mercury into jars and hand them in to the laboratory assistant.

4. After working with mercury, thoroughly wash your hands with soap!

Immediately gather accidentally spilled out drops of mercury with a vacuum cleaner or the clean surface of a zinc plate, or with a brush whose bristles are made from thin copper wire. Transfer the gathered mercury into a special vessel for contaminated mercury on the tray and pour water over it. *Never pour out or discard mercury or ist salts into sinks!*

COMPOUNDS

(The experiments are demonstrated and explained by two students.)

Mercury(I) and Mercury(II) Oxides. 1. Pour 1-2 ml of mercury(I) nitrate into a test tube and add 1 ml of a 1 *N* sodium hydroxide solution. What happens? Does the product dissolve in nitric acid? Write the equations of the reactions.

2. Pour 1 ml of a mercury(II) nitrate solution into a test tube and add with stirring a 1 *N* sodium hydroxide solution up to complete precipitation of mercury(II) oxide. What colour does the precipitate have? Write the equation of the reaction. What happens when mercury(II) oxide is heated?

Mercury(I) and Mercury(II) Salts. Under what conditions can mercury(I) and mercury(II) nitrates be obtained when mercury is dissolved in nitric acid?

1. Put a few crystals of mercury(I) nitrate into a test tube and add 2 ml of distilled water. Why does a turbid solution form? Write the equation of the reaction. Run a similar experiment with mercury(II) nitrate. Under what conditions can a transparent solution of these salts be obtained?

2. Add a sodium chloride solution to one of mercury(I) nitrate. What is the composition of the precipitate? Write the equation of the reaction. Perform a similar experiment with a mercury(II) nitrate solution. Why does no precipitate form in this case? Where are mercury(I) and mercury (II) chlorides used? What other names do they have?

3. Add first a little of a tin(II) chloride solution to one of mercury(I) nitrate, and then an excess of the chloride. What do you observe? Run a similar experiment with mercury(II) nitrate. Write the equations of the reactions. What properties of mercury(I) and mercury(II) compounds are indicated by these reactions?

4. Add hydrogen sulphide water to a solution of mercury(I) nitrate. What forms? Perform a similar experiment with a mercury(II)

nitrate solution. What colour are the precipitates? Write the equations of the reactions. What can mercury sulphide be dissolved in?

Reaction between Mercury(I) and Mercury(II) Salts and an Aqueous Solution of Ammonia. Pour mercury(I) and mercury(II) nitrate solutions into separate test tubes. Add 1 ml of a 1 *N* ammonia solution to each tube. What do you observe? Note the colour of the precipitates. What is their composition? Write the equations of the reactions.

Reaction to Ammonium Ion (Nessler's Reagent). Introduce 5 ml of a 0.1 *N* mercury(II) nitrate solution heated to 80 °C into a 50-ml beaker and add 5 ml of a 0.1 *N* potassium iodide solution. Cool the mixture, let the precipitate settle, pour off the solution, and wash the precipitate three times with cold water by decantation. Add 0.2 g of potassium iodide dissolved in 5 ml of water to the precipitate. When the latter dissolves, pour in 3 ml of a 10% sodium hydroxide solution and transfer the contents into a dark jar.

Pour 2 ml of the solution into a test tube and introduce several drops of a 1 *N* ammonia solution with a pipette. What is obtained? Write the equations of the reactions.

SUPPLEMENTARY EXPERIMENTS AND SYNTHESES

1. Preparation of Zinc Amalgam. *(Perform the experiment on a tray with high sides!)* Put two or three small pieces of pure granulated zinc into a 25-ml porcelain bowl and add 3-4 ml of a 2% mercury(II) nitrate solution acidified with 0.3 ml of concentrated nitric acid. Stir the mixture during 10 minutes, then pour off the solution and wash the zinc with water by decantation until the liquid becomes absolutely transparent. Store the zinc amalgam in a jar under water.

See how zinc amalgam reacts with hydrochloric acid. Touch the zinc amalgam in the acid with a copper wire. What do you observe? What is zinc amalgam used for?

2. Preparation of a Low-Melting Alloy. Put 0.5 g of cadmium, 0.05 g of tin, 1 g of lead, and 2 g of bismuth into a dry test tube. Heat the metal mixture until it melts and cool it. When the alloy solidifies, pour hot water into the test tube. What is observed? At what temperature does the prepared alloy melt? Note the melting point of the individual metals which the alloy is composed of. Explain the observed phenomenon.

3. Preparation of Zinc Chloride. Assemble an apparatus (see Fig. 61), replacing the funnel with a U-tube containing calcium chloride. Weigh 1-2 g of pure granulated zinc in a porcelain boat and place the latter into a refractory tube. Cover the outlet end of the tube

with asbestos to protect the receiver from being heated. A Wurtz tube can be used as the receiver. Fill the calcium chloride tube with phosphoric anhydride applied onto glass wool. While passing a stream of dry chlorine through the apparatus, heat the place of the reaction tube where the boat with zinc is to 650-700 °C. When all the zinc reacts, cool the apparatus in a chlorine stream, next use a Kipp gas generator and displace the chlorine with dry carbon dioxide. Remove the receiver and rapidly close its opening with a stopper.

See what happens to the salt in the air. Transfer a small amount of the product into a porcelain bowl with water. What do you observe? Write the equations of the reactions.

4. **Preparation of Zinc Oxychloride.** Mix 1 g of zinc oxide with a saturated zinc chloride solution containing 1.7 g of anhydrous zinc chloride in a porcelain bowl. Put the mixture onto the lid of a crucible and leave it there for several hours. What occurs? Write the equation of the reaction. What is zinc oxychloride used for?

5. **Preparation of Zinc Chloride Crystallohydrate.** Put 5 g of granulated zinc into a 50-ml flask, pour in 12 ml of water, and add 13 ml of concentrated hydrochloric acid in small portions. When the reaction slows down, place the flask on a warm water bath and bring the reaction up to its end. Let the flask with its contents stand up to your next lesson. Filter the solution, and test it for the presence of iron(II) ions. If the reaction is positive, saturate the solution with chlorine. For what purpose? Tightly close the flask containing the reaction mixture with a stopper and again let it stand up to your next lesson. Heat the flask in a water bath and introduce moist zinc oxide in small portions up to the complete separation of iron hydroxide. How can you determine that the ions of iron have precipitated completely?

Strongly acidify the filtered solution with hydrochloric acid and evaporate it to a syrupy consistence. Next add an equal volume of concentrated hydrochloric acid and let the solution stand for crystallization. Separate the crystals from the mother liquor using a funnel with a glass filtering bottom. What is the composition of the obtained compound? What happens to the salt when heated? What is the reaction of this salt to litmus? Keep the crystals and the mother liquor for following experiments.

Determining the Melting Point of Zinc Chloride Crystallohydrate. Put 1-2 g of zinc chloride crystallohydrate into a test tube, secure the latter in a clamp of a stand, and immerse it into a beaker with water heated to 40 °C. When the salt melts, introduce a thermometer into it (with graduations of 0.1 °C) secured in the stand clamp. Remove the burner and watch the dropping of the temperature. Write down the readings of the thermometer every 30 seconds. Use these data to plot the temperature against the time and establish the melting point of the zinc chloride hydrate.

Prepare zinc bromide and iodide in the same way, using hydrobromic and hydroiodic acids instead of hydrochloric acid.

6. **Use of Zinc Chloride in Soldering.** Clean two copper wire ends with emery paper and place them on a sheet of asbestos so that they are in contact with each other. Put 1-2 g of metallic tin on the asbestos sheet. Heat an electrical soldering iron until it acquires a dark red glow, touch the tin with it, and transfer the drop of molten tin to the place of contact of the copper wires. What do you observe? Did the tin solder the ends of the wires?

Lower the same copper wire for one minute into the mother liquor from which the zinc chloride crystallohydrate crystallized and repeat the above experiment. Did the wires become soldered in this case? What underlies the use of a concentrated zinc chloride solution when metals are soldered? What else can be used to purify a metal?

7. **Preparation of Zinc Iodide in Absolute Ether.** Assemble an apparatus (see Fig. 119*a*), replacing dropping funnel *4* with a glass stopper provided with a ground-glass joint. Put 3 g of powdered zinc, 5.5 g of freshly sublimed iodine, and 50 ml of absolute ether into flask *1*.

Heat the flask until the reaction mixture boils *(use an electric stove with an enclosed coil and insulate the stove surface from the flask with a piece of asbestos!)*. After the complete disappearance of the iodine colour (in 2-2.5 h), pour the solution into a round-bottomed flask provided with a gas-discharge tube having a stopcock (see Fig. 119*b*). Connect the flask via a cooled receiver to a water-jet pump, distil off the major part of the ether at room temperature, after which carefully heat the flask in a sand bath. Transfer the substance into a weighed weighing bottle. Weigh it and calculate the yield in per cent.

8. **Preparation of Zinc Oxyacetate.** Put 12.5 g of zinc carbonate into a porcelain bowl and add 30 ml of glacial acetic acid. While thoroughly stirring, evaporate the mixture on a water bath until dry. Again add 30 ml of glacial acetic acid to the dry residue and evaporate until dry.

Transfer the product into a glass test tube with a standard ground-glass joint. Connect the tube via the joint to a vacuum pump (Fig. 138). Heat the tube with the substance in a crucible electrical furnace to 120-130 °C. Hold the substance at this temperature and in a vacuum of 10^{-1} mmHg during 30 min. After this, raise the temperature to 300-320 °C. Under these conditions, continue evacuation for 10-15 min. Gather the crystals deposited in the cold zone of the test tube. Transfer them into a weighed weighing bottle, weigh the substance, and calculate the yield in per cent. Examine the shape of the crystals under a microscope. What is the structure of a zinc oxyacetate molecule?

9. Preparation of Crystalline Cadmium Sulphide. Dissolve 3 g of cadmium sulphate in 80 ml of water, add 20 ml of a 1 N sulphuric acid solution to the reaction vessel, and pass a stream of hydrogen sulphide through it up to complete precipitation of cadmium sulphide. Filter off the cadmium sulphide precipitate, wash it several times with water saturated with hydrogen sulphide, remove it from the filter, and dry it in a drying cabinet at 100 °C.

Prepare a thoroughly ground mixture of 1 g of the cadmium sulphide obtained previously, 5 g of sulphur, and 5 g of potassium carbonate. Transfer the mixture into a porcelain crucible, and fuse it at the lowest possible temperature. Next cool the crucible and treat the product with water. Separate the prepared cadmium sulphide crystals and examine their shape with a magnifying glass.

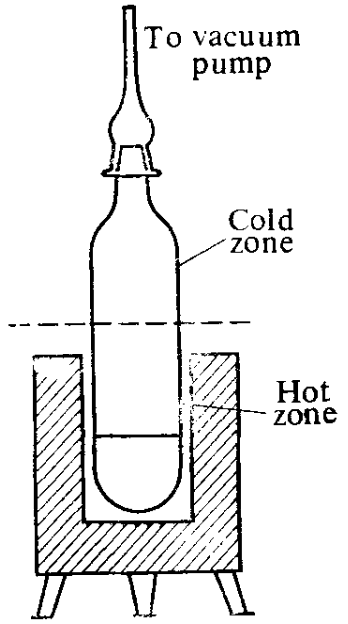


Fig. 138. Glass test tube for purifying zinc oxyacetate in vacuum

10. Preparation of Autocomplex Cadmium Iodide. Pour 20 ml of a 10% cadmium sulphate solution into a test tube and lower a plate of metallic zinc into it. What do you observe?

After an hour, extract the unreacted zinc. Filter off the separated metal through a paper filter, wash it with hot water, and dry it in the air.

Put 2.8 g of iodine, 2.4 g of the freshly precipitated cadmium powder, and 20 ml of water into a 50-ml flask provided with a vertically arranged cooler. Boil the reaction mixture up to complete dissolution of the reactants. Next remove the cooler and boil the contents of the flask until the excess iodine is removed (*in a fume cupboard!*) Evaporate the transparent solution in a water bath until crystals appear, filter off the latter through a paper filter, and rinse them with small portions of cold water. What is the composition of the formed substance?

Dissolve a small amount of the crystals in distilled water and add a few drops of silver nitrate. Does silver iodide precipitate? Write the equation of the reaction.

11. Preparation of Cadmium Pigments. Place two thin layers (from 0.5 to 1 g) of cadmium carbonate spaced 6 cm apart into the middle part of a refractory glass tube 40 cm long and 5 cm in diameter and pass a stream of hydrogen sulphide through the tube. When the colour of the first layer changes, heat the place of the reac-

tion tube where the second cadmium carbonate layer is to 600-700 °C. What is observed? What causes the change in the colour of the preparation? Write the equations of the reactions. How are cadmium pigments prepared?

12. Purification of Mercury by Filtration. Take a smooth paper filter, puncture its cone three or four times with an ordinary needle, and put it into a glass funnel. Put the latter with the filter into a cylinder and transfer 5-6 ml of contaminated mercury onto the filter. What happens? What impurities are removed from mercury in this way?

13. Chemical Purification of Mercury. Pour all the mercury purified in the preceding experiment into a 100-ml separatory funnel, and add 20 ml of a 5% mercury(I) nitrate solution acidified with 2 ml of a 10% nitric acid solution. Close the opening of the funnel with a stopper and shake it for 10-15 minutes. Next pour the mercury out of the funnel through a stopcock into a cylinder, pour the washing liquid out of the funnel, and wash the latter two or three times with distilled water. Again transfer the mercury from the cylinder into the funnel and wash it two or three times with distilled water. Drain off the metal into a clean reagent jar, remove the water droplets from the surface of the mercury with pieces of filter paper, tightly close the jar with a stopper, and let it stand on the tray. What impurities was the mercury cleaned from in this case?

14. Preparation of Mercury(I) Nitrate. Put 1 g of metallic mercury into a test tube and add 1.5 ml of a 25% nitric acid solution. Let the reaction mixture stand for one or two hours until crystals form. Why is this experiment run in excess metallic mercury? Write the equation of the reaction.

15. Preparation of Mercury(II) Nitrate. Pour 5 ml of a 25% nitric acid solution onto 0.5 g of metallic mercury and slightly heat the reaction mixture. What happens? Dilute the solution with water and filter it if required. Evaporate the filtrate slightly in a porcelain bowl in a water bath, cool it, and let it crystallize. Filter off the crystals through a paper filter and dry them in the air at room temperature. What is the composition of the prepared salt? Why is an excess of nitric acid used in this case?

16. Preparation of Mercury(II) Iodide. Prepare a 0.02 *N* solution of mercury(II) nitrate. Boil 2-3 ml of the solution, add an equal volume of a 0.02 *N* potassium iodide solution, and let the mixture stand to your next lesson. Filter off the precipitate (what is its composition?) through a paper filter, wash it with water, and dry it in a drying cabinet at 70 °C. What happens to the salt when it is kept in the air?

30 TIN, LEAD

Write the electron configurations of tin and lead atoms. Give examples of compounds in which tin and lead exhibit various oxidation states. Give a general and comparative characteristic of Group four elements of Mendeleev's periodic table.

30.1 TIN

Write the equations of the reactions between tin and nitric, sulphuric, and hydrochloric acids under various conditions (temperature, concentration). Does tin dissolve in solutions of alkalies?

Macrocrystalline Tin. Suspend a strip of tin foil 5-8 cm long vertically in a 100-ml beaker. Pour 20 ml of distilled water into the beaker. Take with a pipette the same amount of a concentrated tin(II) chloride solution acidified with hydrochloric acid, lower the bottom edge of the pipette to the bottom of the beaker, and carefully pour in this solution so that two layers form. Observe the occurring phenomenon. In which of the two liquid layers do crystals grow?

Preparation of Tin by Reduction with Zinc. Immerse a plate of metallic zinc into a tin(II) chloride solution. What happens? Write the equation of the reaction.

Tin(II) and Tin(IV) Hydroxides. Prepare tin(II) and tin(IV) hydroxides in separate test tubes from solutions of tin chlorides. What reagent should be used to precipitate the tin hydroxides? Do tin hydroxides exhibit amphoteric properties? What tin compounds are known as α- and β-stannic acids? How are they prepared? Write the equations of the reactions.

Sodium Stannite. Add an excess of sodium hydroxide solution in small portions to a tin(II) chloride solution. Comment on your observations.

Precipitate bismuth hydroxide, and introduce it into a sodium stannite solution. What happens? Write the equations of the reactions. What properties of tin(II) compounds are indicated by this reaction?

Prepare a sodium stannite solution, dilute it with water, and let it stand to your next lesson. What happens? How can sodium stannite be prepared in an aqueous solution and by a dry technique? Is the composition of the sodium stannite obtained in both cases the same? Write the equations of the reactions.

Properties of Tin(II) Chloride. 1. Acquaint yourself with the ways of preparing tin(II) and tin(IV) chlorides (see Supplementary Experiments and Syntheses 5 and 6, p. 268). Which of these compounds should hydrolyze to a greater extent?

2. Pour 1-2 ml of a tin(II) chloride solution into each of two test tubes. Add a little bromine water to the first tube. How does the colour of the solution change? Add sulphurous acid to the second tube. What do you observe? Write the equations of the reactions. What properties of tin(II) compounds do these reactions indicate?

Tin(II) and Tin(IV) Sulphides. Pass a stream of hydrogen sulphide through hydrogen chloride solutions of tin(II) and tin(IV) chlorides in separate test tubes. What is the colour of the sulphide precipitates? Write the equations of the reactions.

Explain the different reaction of ammonium sulphide and polysulphide with tin(II) sulphide and tin(IV) sulphide.

30.2 LEAD

Lead compounds are poisonous, therefore after running experiments with lead compounds thoroughly wash your hands with warm water and soap.

Preparation of Lead by Displacement with Zinc. Pour several millilitres of a lead acetate solution into a test tube and lower a zinc plate into it. What is observed? Write the equation of the reaction. In which acids does lead dissolve best of all?

OXIDES AND HYDROXIDES

What is the composition of litharge, massicot, lead(IV) oxide, and minium? Under what conditions do they form? What is their structure? What are the oxidation states of lead in these oxides?

1. Put a small amount of lead(II) oxide into one test tube, of lead(IV) oxide into a second one, and of minium into a third one. Pour 3-5 ml of concentrated hydrochloric acid into each of the tubes. Stir their contents and heat them. What do you observe? What gas evolves. Write the equations of the reactions. What properties do lead(IV) oxide and minium exhibit in this reaction?

2. Perform a similar experiment, using a 10% nitric acid solution instead of the hydrochloric acid. Write the equations of the reactions.

3. Introduce 0.5 g of lead(IV) oxide into a 0.1 N manganese sulphate solution acidified with a 10% sulphuric acid solution and heat it. Let the precipitate settle. What is the change in the solution's colour due to? Write the equation of the reaction. Will a similar reaction proceed with lead(II) oxide and minium?

Lead(II) and Lead(IV) Hydroxides. What properties do lead(II) and lead(IV) hydroxides have? Write the formulas of sodium plumbites formed in aqueous solutions and prepared by a "dry" technique.

SALTS AND THEIR PROPERTIES

Lead Iodide. Add a potassium iodide solution to one of lead acetate. What is observed? Pour off a part of the solution with the precipitate (about 1 ml) into a beaker, add 10-15 ml of water acidified with acetic acid, and heat the solution. What is its colour? Cool the solution. Explain the observed phenomena. Compare the solubility of lead iodide and chloride in water. How does it change with the temperature?

Basic Lead Carbonate (White Lead). Dissolve 1 g of lead acetate in 6 ml of water, introduce 0.5 g of lead(II) oxide into the solution in small portions while stirring it, and heat the mixture. What happens?

Pass a stream of carbon dioxide into the basic lead acetate solution obtained. What is the composition of the precipitate? Write the equations of the reactions.

What is the composition of zinc white and titanium white? Which white paint has better properties—a better hiding ability and an unchanging colour—when exposed to the air for a long time? Under what conditions is normal lead carbonate prepared (compare with magnesium carbonate)?

Lead Sulphide. Prepare lead sulphide by precipitating it from an aqueous solution of lead acetate, pour the solution off the precipitate, and treat the latter with a dilute nitric acid solution. What is obtained? Write the equations of the reactions and explain their course.

Add hydrogen peroxide to the lead sulphate precipitate in a test tube and shake it vigorously. What changes do you observe? Write the equation of the reaction. Does lead form sulphosalts? Why is lead acetate, and not another salt, used in all the reactions?

SUPPLEMENTARY EXPERIMENTS AND SYNTHESES

1. **Preparation of Tin by Reduction with Charcoal.** Prepare a mixture of 2.5 g tin(IV) oxide, 1 g of charcoal, and 0.5 g of ammonium carbonate. Transfer the mixture into a crucible and roast it in a muffle furnace. Write the equation of the reaction. Transfer the obtained bead into another crucible and fuse it with borax. After cooling, break the crucible and wash off the borax with hot water.

2. **Preparation and Properties of Tin(II) Oxide.** Add an aqueous solution of ammonia to 10 ml of a tin(II) chloride solution up to the complete precipitation of tin(II) hydroxide. Pour off the mother liquor, wash the precipitate by decantation, filter it off, and dry it in a drying cabinet at 70-80 °C.

Place dry tin(II) hydroxide in a porcelain boat into a refractory tube connected to a Kipp gas generator charged with marble and hydrochloric acid. Displace the air from the apparatus with a stream of dry carbon dioxide, and by gradually heating the tube with the flame of a gas burner, roast the tin(II) hydroxide up to the complete removal of water vapour.

When the substance is dehydrated, remove the boat and spill out the tin(II) oxide into a heated porcelain bowl. What do you observe? What is the colour of tin(II) and tin(IV) oxides? What oxidation state do the most stable tin compounds correspond to?

3. **Preparation of α-Stannic Acid.** Add a 10% ammonia solution to a tin(IV) chloride one up to complete precipitation. Wash the product with water by decantation until the chloride ions are removed and filter it off on a Büchner funnel. Test the reaction of α-stannic acid with water, acids, and alkalies. Do the properties of this acid remain the same after prolonged standing or boiling? Perform the relevant experiments.

4. **Preparation of β-Stannic Acid.** Treat 0.5 g of tin with a 40-50% nitric acid solution with heating. What do you observe? Thoroughly wash the precipitate with water by decantation. See how β-stannic acid reacts with alkalies and acids. Compare the chemical activity of α- and β-stannic acids.

5. **Preparation of Tin(II) Chloride.** Put 2 g of tin into a porcelain bowl and treat it while heating with 20 ml of a 24% hydrochloric acid solution. Put small pieces of platinum into the bowl. Why does the tin dissolve more rapidly in the presence of platinum?

Evaporate the solution up to the beginning of crystallization. Filter off the crystals. What is their composition? Write the equation of the reaction. Study the properties of tin(II) chloride.

6. **Preparation of Tin(IV) Chloride.** Assemble an apparatus as shown in Fig. 139 and thoroughly dry it (for what purpose?). Put 4-5 g of metallic tin or 6-8 g of anhydrous tin(II) chloride into 25-ml Wurtz flask *1*. Pass a stream of dry chlorine through the apparatus. When flask *1* becomes filled with chlorine, slightly heat it. What do you observe? Continue heating if the reaction stops. What is the colour of tin(IV) chloride due to? How can it be purified?

Determine the boiling point of tin(IV) chloride (see Fig. 20). Distil off the tin(IV) chloride into a drawn out test tube and (*carefully, wear eye protection!*) seal it. Test how tin(IV) chloride reacts with water.

7. **Preparation of Chlorostannic Acid.** Pour concentrated hydrochloric acid into tin(IV) chloride in a proportion of 28 parts by mass of hydrogen choride to 100 parts by mass of the tin chloride. Cool the solution and pass a stream of dry hydrogen chloride into it until its absorption stops. Test the reaction of chlorostannic acid with

water. Add a solution of a potassium salt to one of chlorostannic acid. What do you observe? Write the equation of the reaction.

8. **Preparation of Ammonium Chlorostannate.** Prepare a 60% tin(IV) chloride solution in concentrated hydrochloric acid and add to it a warm saturated solution containing an equimolecular amount of ammonium chloride. Cool the solution with a mixture of ice and sodium chloride, filter off the crystalline precipitate using a glass filter No. 3, and wash the precipitate on the filter with the smallest possible amount of concentrated hydrochloric acid cooled to 0 °C.

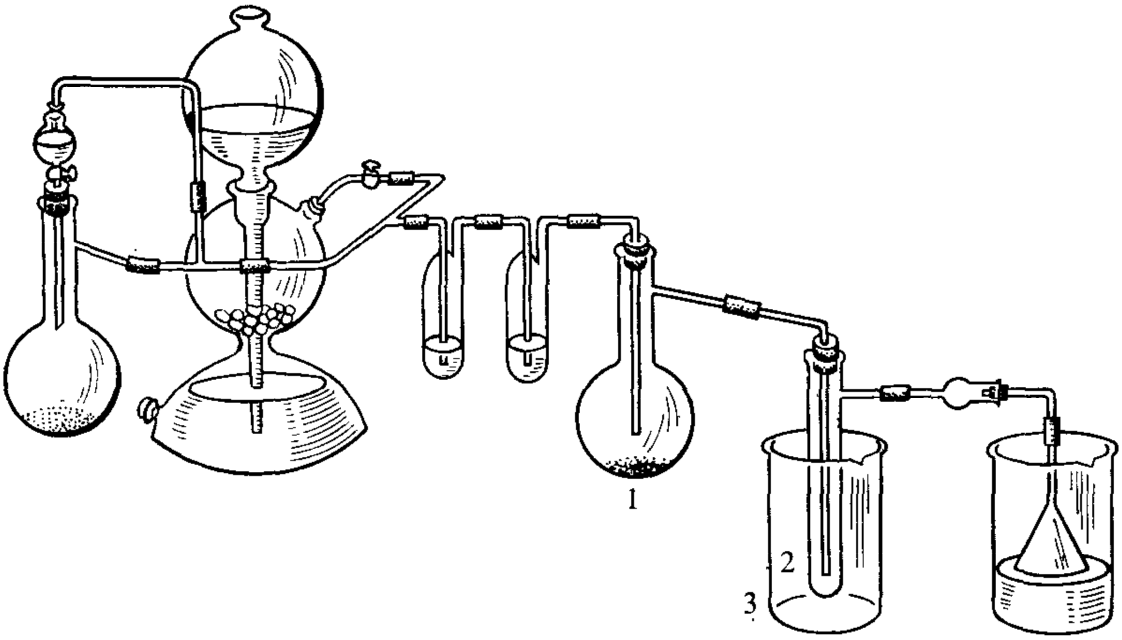


Fig. 139. Apparatus for preparing tin(IV) chloride

Dry the compound in the air, next transfer it into a previously weighed weighing bottle, weigh it, and calculate the yield in per cent.

9. **Soldering.** *Preparation of a Low-Melting Solder (Quick Solder).* Weigh 6.3 g of tin and 3.7 g of lead on a technical chemical balance. Transfer the lead into an iron bowl or porcelain crucible and heat it up to complete melting, then add the tin. What are the melting points of tin and lead? Carefully mix the alloy with an iron rod and then pour it into a wooden or iron mould. Check the melting point of the alloy. Acquaint yourself with the melting diagram of the lead-tin system.

Preparation of Metal Surfaces for Soldering. Prior to soldering, thoroughly clean the surface of the metal with a file or emery paper. Such surface cleaning is not needed when soldering tinplate. Large metallic surfaces to be soldered should first be tinned. To do this, heat the metal article on the flame of a burner (300-350 °C), spread ammonium chloride over the surface to be soldered (for what purpose?), put a piece of tin on it, and spread the tin over the metal surface with an asbestos wad.

Preparation of the Soldering Iron. Clean the surface of the soldering iron bit (tip). To do this, heat the iron and then press it firmly against a piece of ammonium chloride. Touch a piece of solder with the cleaned end of the soldering iron. If the surface of the bit is clean, the solder readily "tins" the iron.

Preparation of a "Soldering" Solution (Flux). Dissolve 4 g of zinc chloride (the anhydrous salt) and 1.5 g of ammonium chloride in a small amount of water. Add water up to 100 ml. What is this solution used for?

Soldering. Wet the surfaces to be soldered (the seam) with the soldering solution. Heat the soldering iron to a temperature higher than the melting point of the solder. If the soldering iron being used is not an electrical one, heat it from its blunt end until the flame acquires a green colour. Press the bit of the iron against a piece of ammonium chloride or immerse it for an instant into a bowl with the soldering solution; rosin can also be used. Touch a piece of solder with the iron, pick up a small amount of the solder, and bring it into contact with the seam, moving it to and fro while slightly pressing on the iron up to uniform distribution of the solder. If large surfaces are being soldered, it is better to preliminarily fasten them with wire. Let the solder cool completely because at a temperature close to its solidification point solder is very brittle. Excess solder can be removed with a file.

10. Preparation of Lead. *a.* Thoroughly mix 5 g of lead(II) oxide and 0.5 g of finely ground charcoal. The lead(II) oxide must be preliminarily dried in a drying cabinet at 100 °C, and the charcoal roasted in an iron crucible covered with a lid. Put the mixture into a porcelain crucible, spill charcoal over it, and roast it in a muffle furnace at 800 °C. After 10 or 15 minutes, mix the contents of the crucible with a carbon rod and again roast them during 30 minutes. Pour out the molten lead onto a chamotte dish. Cool the metal bead and keep it for following experiments. Calculate the yield in per cent. Write the equations of the reactions.

b. Pour a little lead acetate solution into a test tube and lower a narrow zinc strip into it. What is observed? Write the equation of the reaction.

11. Properties of Lead. Heat a small piece of metallic lead in a porcelain crucible with the flame of a gas burner. What changes are observed? Write the equation of the reaction.

Test the reaction of dilute and concentrated hydrochloric, nitric, and acetic acids, and also of a 10% sodium hydroxide solution with metallic lead (in the cold and with heating). Explain the occurring phenomena and write the equations of the reactions.

12. Preparation of Lead(II) Oxide (Yellow and Red Modifications). Fill two small boats with lead carbonate and roast them in a stream of dry nitrogen, one at 490 °C and the other at 650 °C until carbon

dioxide stops evolving. What substances are obtained? In what do they differ from each other? What is the application of lead(II) oxide in engineering? Test the reaction of lead(II) oxide with solutions of acetic and nitric acids and an alkali solution. Write the equations of the reactions.

13. Preparation of Lead(II) Acetate (Lead Sugar). Dissolve 3 g of lead(II) oxide in a calculated amount of a hot 50% acetic acid solution. Filter the solution, and add 1 ml of acetic acid with the same concentration to the filtrate. Evaporate the latter up to half of its initial volume and let it stand for crystallization. Separate the crystals from the mother liquor on a Büchner funnel and wash them with small portions of ethanol, and then with ether (for what purpose?). What is the composition of the product?

Heat a small part of the crystals in a dry test tube, first carefully, and then more strongly (280 °C). What happens to the lead acetate in the air and when heated? Can lead sugar be dried in a desiccator over sulphuric acid?

Wet several strips of filter paper with a lead acetate solution, put them on glass, and let them dry in the air. Introduce the dried paper into the flame of burner. What happens? What is lead acetate used for? Keep the remaining salt for following experiments.

14. Preparation and Properties of Lead(IV) Oxide. a. Prepare a saturated transparent solution of chlorinated lime and a solution of 3 g of lead acetate in 5 ml of water. Add an equal volume of a lead acetate solution heated to 50 °C to the first solution while stirring it. Heat the reaction mixture to 100-110 °C. Wash the precipitate first with water by decantation, and next with a dilute nitric acid solution (what ions are washed off here?). Filter off the product, again wash it two or three times on the funnel with water and dry it at 100 °C. Keep the preparation. Write the equation of the reaction.

b. Spill a little lead(IV) oxide into a hydrogen peroxide solution. Explain the observed phenomenon.

c. Introduce a little lead(IV) oxide into a 0.1 *N* manganese sulphate solution acidified with a 10% sulphuric acid solution and heat it. Explain the change in the solution's colour. What properties does lead(IV) oxide have? Write the equation of the reaction. Can manganese sulphate be replaced with the chloride to run this experiment?

15. Preparation and Properties of Red Lead Oxide (Minium). a. Roast 2-3 g of lead carbonate at 450-500 °C in a porcelain bowl. When decomposition of the salt terminates, roast the substance at the same temperature for another two or three hours. Next transfer the product into a beaker and boil it several times with a lead acetate solution. Pour off the solution from the precipitate, filter off the latter, wash it with hot water, and dry it in a drying cabinet at

100 °C. What is the appearance and composition of the substance? Write the equation of the reaction.

b. Heat 0.5 g of the red lead oxide prepared in the preceding experiment in a refractory test tube first carefully, and then at 600 °C. Lower a glowing splinter into the tube. How does red lead oxide behave when roasted? Write the equation of the reaction. At what temperature can oxygen of the air combine with lead(II) oxide?

c. Add concentrated hydrochloric acid to a small amount of red lead oxide in a test tube. What is obtained? Write the equation of the reaction.

16. Preparation of Ammonium Hexachloroplumbate. Grind 2.5 g of lead chloride in a mortar with 5 ml of concentrated hydrochloric acid (*in a fume cupboard!*). Pour the formed solution together with the suspension of fine crystals into a beaker, again grind the lead chloride remaining in the mortar with hydrochloric acid, and so on. To extract the lead chloride, 50 ml of concentrated hydrochloric acid are needed. Transfer the solution from the beaker into two wash bottles and pass a stream of chlorine through them during two or three hours. Filter off the undissolved precipitate. Pour the filtrates into a 100-ml flask. Cool the contents of the flask to 0 °C, and next add a solution of 2 g of ammonium chloride in 20 g of water also cooled to 0 °C. Let the flask stand for two or three hours in a cooling mixture. Transfer the crystals separated from the solution onto a funnel with a porous glass bottom, filter them off, wash them with 10 ml of cooled ethanol, and dry them in a drying cabinet at 50 °C. Transfer a small amount of the crystals into a test tube and treat them with water. What do you observe? Write the equations of the reactions. Keep the salt for preparing lead tetrachloride.

17. Preparation of Lead Tetrachloride. Thoroughly mix 1 g of ammonium hexachloroplumbate with 3 g of concentrated sulphuric acid cooled to 0 °C. Separate the heavy drops of oily liquid formed from the reaction mixture. What are these oily drops? Write the equations of the reactions.

18. Preparation of Lead Tetraacetate. Assemble an apparatus (see Fig. 119*a*), replacing the cooler with a thermometer. Pour 55 ml of glacial (frozen out twice) acetic acid and 17 ml of freshly distilled acetic anhydride ($d^{20} = 1.0820$) into three-neck flask *1*. Heat the mixture in the flask in a water bath up to 40 °C. Stop the heating and introduce 30 g of red oxide (minium) from test tube *4* in small portions while vigorously stirring. Preliminarily triturate the red lead oxide and thoroughly dry it at 200 °C for 2.5 hours. Introduce the oxide into the flask at a rate such that the temperature of the reaction mixture does not rise above 50 °C. Why? If the flask does get heated strongly, cool it in a bath with cold water, and when the temperature lowers heat it to 50 °C to complete the reaction.

Cool the reaction mixture in the flask to 0 °C. Disconnect mixer *3*

from the flask, close its neck with a stopper, remove test tube *4*, and rapidly decant the mother liquor from the crystals. Filter off the crystals using a Büchner funnel in a stream of dry nitrogen (see Fig. 64*b*). Rinse the crystals with glacial acetic acid and dry them in a desiccator over phosphoric anhydride. Transfer the substance into a weighed weighing bottle and weigh it. Calculate the yield in per cent.

To produce an additional amount of the lead tetraacetate, again transfer the mother liquor into flask *1* and pass a stream of dry chlorine through it, heating the solution to 80 °C with thorough stirring. Pass the chlorine through the flask until lead chloride crystals stop separating.

Separate the precipitate using a funnel for hot filtration. Cool the filtrate to 0 °C. Separate the crystals formed as described above and combine them with the first portion.

31 ARSENIC, ANTIMONY, BISMUTH

Write the electron configurations of the arsenic subgroup elements. Find the values of the standard electrode potentials of these elements. In what acids and under what conditions do they dissolve?

31.1 ARSENIC

Perform all the experiments in the presence of your instructor. Arsenic compounds are very poisonous even in minimal doses! Perform all work with arsenic compounds in a fume cupboard! Pour residues of solutions into special jars and hand them in to the laboratory assistant. After completing work, thoroughly wash the ware in which the experiments were run. Wash your hands with soap.

Preparation of Arsenic. Put a small amount of a mixture of arsenous acid anhydride with coal into a short glass tube sealed at one end and heat the mixture strongly in the flame of a burner. What do you observe? Write the equation of the reaction.

Preparation of Arsenic Hydride (Arsine). *Perform this experiment only if there is a strong draught in the fume cupboard!*

To prepare arsenic hydride, assemble an apparatus as shown in Fig. 140 and perform this experiment as described under the heading "Preparation of Antimony Hydride" in Sec. 31.2. Write the equations of all the reactions proceeding in this experiment and explain them.

Arsenous Acid Anhydride. 1. Pour 2-3 ml of water into a test tube, add about 0.1 g of arsenous acid anhydride, and heat the reaction mixture. Does the arsenous acid anhydride dissolve complete-

ly? Write the equation of the reaction. Divide the contents of the test tube into two parts and keep them for the following experiments.

2. Add a sodium hydroxide solution to one part of the obtained mixture and heat it. What happens? Write the equation of the reaction.

3. Treat a part of the liquid containing the arsenous acid anhydride with 3-4 ml of concentrated hydrochloric acid and heat the mixture (*in a fume cupboard!*). What do you observe? Identify the solute.

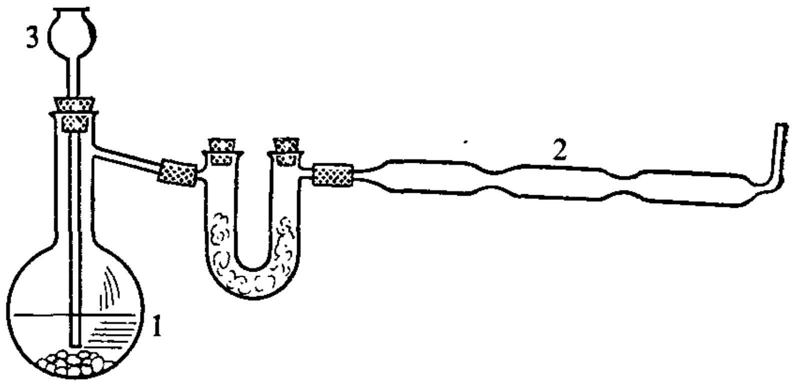


Fig. 140. Apparatus for preparing antimony hydride

What ions are present in an aqueous solution of arsenous acid anhydride? Write the equations of the reactions.

4. Pour a sodium arsenite solution into two test tubes, add a silver nitrate solution to one of them and iodine water to the other. What is observed? Write the equations of the reactions. What properties of arsenous acid are revealed by the performed experiments?

Arsenic Acid. Put 0.1 g of arsenous acid anhydride into a porcelain bowl with 5 ml of concentrated nitric acid and heat the mixture (*in a fume cupboard!*) on the small flame of a burner until the evolution of nitrogen oxides terminates and the arsenous acid anhydride dissolves completely. By adding water and evaporating until dry (on a small burner flame), remove the excess nitric acid. What is the composition of the solid product? Write the equation of the reaction.

Dissolve the product in water and treat the solution with silver nitrate. What is the composition of the precipitate? Write the equation of the reaction.

Arsenic(III) and Arsenic(V) Sulphides. Pass a stream of hydrogen sulphide into sodium arsenite and sodium arsenate solutions. What happens? Run similar experiments with acidified solutions of the same salts. What do you observe in this case? Write the equations of the reactions and explain the occurring phenomena.

Arsenic(III) and Arsenic(V) Thiosalts. Filter off the arsenic sulphides obtained and test their solubility separately in ammonium

sulphide and polysulphide. Write the equations of the reactions. What is observed when the solutions are acidified with hydrochloric acid? Write the equations of the reactions.

31.2 ANTIMONY

Preparation of Antimony Hydride (Stibine). (The experiment is prepared by one student and demonstrated to the class.) *Perform the experiment in a fume cupboard!* To prepare antimony hydride, assemble an apparatus (Fig. 140). Put 25-30 small pieces of granulated zinc and 50-70 ml of a 20% sulphuric acid solution into Wurtz flask *1*. After all the air is displaced from the apparatus (test the purity of the hydrogen), heat the middle of refractory tube *2*. Does a deposit form on the glass? Light the evolving hydrogen and put the lid of a crucible in the hydrogen flame. What is observed? Explain the significance of these preliminary tests.

Extinguish the burning hydrogen and when the apparatus cools, introduce 1-2 ml of an antimony compound solution into flask *1* via funnel *3*. Again test the purity of the hydrogen evolving from the apparatus. Light the hydrogen evolving from the apparatus and heat the tube at its middle. What do you observe? What is the colour of the flame? Hold a crucible lid in the flame, and give attention to the antimony deposit formed on it. Treat the substance obtained on the crucible lid with a solution of sodium hypochlorite or calcium hypochlorite (chlorinated lime). What is observed? Does arsenic dissolve under these conditions? Write the equations of all the reactions proceeding in this experiment and explain them.

Compare the properties of antimony hydride with those of similar compounds of arsenic, phosphorus, and nitrogen (the thermal stability, reducing properties, etc.).

Antimony(III) Oxide. 1. Take 10 ml of an antimony trichloride solution acidified with hydrochloric acid and add a sodium carbonate solution up to a weakly alkaline reaction. What is observed? Heat the reaction mixture until the carbon dioxide bubbles stop evolving. Let the precipitate settle, and wash it several times with hot water by decantation.

2. Test the reaction of antimony(III) oxide with water, solutions of hydrochloric and tartaric acids, and also with solutions of alkalies. Write the equations of the reactions. Is antimony(III) oxide acidic, amphoteric, or basic?

3. Test a sodium antimonite solution with silver nitrate. What precipitates? What properties does antimony(III) exhibit in this reaction?

Properties of Antimony(V) Oxide. Put a little antimony(V) oxide into two test tubes and test its reaction with a 10% sodium hydroxide solution and with concentrated hydrochloric acid. What do you

observe? Write the equations of the reactions. In what way can antimony(V) oxide be prepared?

Antimony(III) and Antimony(V) Sulphides and Thiosalts. Prepare antimony(III) and antimony(V) sulphides and see how they react with ammonium sulphide and polysulphide. Write the equations of the reactions. What happens when the prepared solutions of antimony thiosalts are acidified?

31.3 BISMUTH

Preparation. Prepare bismuth by reducing a solution of its salt with zinc and test the reaction of the bismuth prepared with acids. Under what conditions can bismuth be prepared from its compounds by using tin(II) compounds as the reducing agent? Write the equations of the reactions.

Properties of Bismuth(III) Compounds. 1. What happens when bismuth salts react with water? How can transparent solutions of bismuth(III) salts be prepared?

2. Prepare bismuth(III) hydroxide and bismuth(III) sulphide and study their properties. Does bismuth form thiosalts? Write the equations of the reactions.

Preparation and Properties of Bismuth(V) Compounds. 1. Precipitate bismuth(III) hydroxide in a test tube and treat it with a saturated potassium persulphate solution (2-3 ml) while heating it. What happens? Write the equation of the reaction. Wash the precipitate three times with water by decantation.

2. Prepare a solution containing one or two drops of a 10% manganese nitrate solution, one or two drops of a concentrated nitric acid solution, and two or three drops of water in a test tube. Cool the solution and introduce a potassium bismuthate powder into it. What do you observe? What properties of bismuth(V) compounds does the given reaction indicate? Write the equation of the reaction.

Compare the acid-basic, reducing, and oxidizing properties of arsenic, antimony, and bismuth hydroxides.

SUPPLEMENTARY EXPERIMENTS AND SYNTHESES

1. Preparation of Antimony. Put a thoroughly dried mixture of 12 g of antimony sulphide, 5 g of reduced powdered iron, 1.5 g of sodium sulphide, and 0.5 g of powdered charcoal into a chamotte or porcelain crucible and roast it in a muffle furnace at 800 °C. After the entire mixture softens, continue the heating for another 20-30 minutes. Next cool the crucible, break it, and extract the antimony bead.

Test the reaction of metallic antimony with hydrochloric, sulphuric, and nitric acids. What position does antimony occupy in the electrochemical series of the metals?

2. Preparation of Antimony(V) Oxide. Treat 0.25 g of powdered metallic antimony with 2-3 ml of concentrated nitric acid in a porcelain bowl while heating it in a water bath. Consider oxidation to be completed if a sample of the obtained white powder dissolved in an alkali will not reduce an ammonia solution of silver. When oxidation is completed, dilute the reaction mixture with water and separate the precipitate by decantation. Dry the precipitate in a water bath until it is dry, and then in a sand bath (275 °C). What is observed when it is treated with concentrated hydrochloric acid and a sodium hydroxide solution? Write the equations of the reactions. How can antimony(III) oxide be prepared?

3. Preparation of Antimony(III) Iodide. (*Perform the experiment in the presence of your instructor in a fume cupboard, away from a flame!*) Assemble an apparatus (see Fig. 119*a*). Place 1 g of finely triturated metallic antimony into a three-neck flask and add 25 ml of benzene. Prepare a solution of 4 g of iodine in 75 ml of benzene and pour it into dropping funnel *4*. Heat the mixture in flask *1* in a water bath with stirring until it boils (*use an electrical stove with an enclosed coil!*).

Drop in the iodine solution from dropping funnel *4* while heating. Continue the heating for another 1-1.5 hours up to complete dissolution of the antimony. Let the solution stand overnight in the apparatus and on the following day filter off the crystals of antimony(III) iodide. If no crystals precipitated and unreacted antimony remains, heat the solution and filter it while hot through a paper filter on a funnel for hot filtration.

Evaporate the solution (*in a fume cupboard, away from a flame!*) on a water bath until a film appears. Cool the solution to room temperature. Filter off the formed crystals using a glass filter No. 3.

Put the antimony(III) iodide crystals in a porcelain boat into the end of a quartz tube (60-70 cm long) heated by a tubular electric furnace. Pass a stream of dry carbon dioxide (nitrogen or argon may also be used) through the tube, raise its temperature to 200 °C, and maintain it during 30-40 minutes. Cool the apparatus and transfer the crystals gathered in the cold end of the tube into a weighed weighing bottle, weigh it, and calculate the yield in per cent.

4. Preparation of Bismuth and Studying of Its Properties. (*Perform the experiment in the presence of your instructor, wear eye protection or a protective mask!*) Prepare bismuth by reducing 0.5 g of bismuth(III) oxide with hydrogen similar to the preparation of metallic nickel or iron. Perform the reduction at 240-270 °C.

See how the bismuth prepared reacts with dilute and concentrated hydrochloric, sulphuric, and nitric acids.

APPENDIX 1. SELECTED TABLES

Table 1. SOLUBILITY OF SALTS IN 100 g OF SOLUTION CALCULATED FOR THE ANHYDROUS SALT

t, °C	Amount of anhydrous salt, %	Solid phase
	$Al_2(SO_4)_3$	
0	23.8	
10	25.1	
20	26.6	
30	28.8	$Al_2(SO_4)_3 \cdot 18H_2O$
40	31.4	
50	34.3	
60	37.1	
80	42.2	
100	47.1	
	NH_4NO_3	
0	54.2	
20	63.9	
30	70.8	
40	74.8	NH_4NO_3
50	78.0	
60	80.2	
70	83.7	
80	85.9	
90	88.1	
100	91.0	
	$(NH_4)_2SO_4$	
0	41.4	
10	42.2	
20	43.0	
30	43.8	$(NH_4)_2SO_4$
40	44.8	
50	45.8	
60	46.8	
70	47.9	
80	48.8	
90	49.8	
100	50.8	
	NH_4Cl	
0	23.0	
10	25.1	
20	27.1	
30	29.3	NH_4Cl
40	31.5	
50	33.5	
60	35.6	
70	37.6	
80	39.6	
100	43.6	
	NH_4HCO_3	
0	10.9	
10	13.7	NH_4HCO_3
20	17.5	
30	21.3	
40	24.2	
50	30.0	
	$(NH_4)_2CO_3$	
15	20.0	
20	22.5	$(NH_4)_2CO_3 \cdot H_2O$
30	27.2	
50	33.5	
	$FeSO_4$	
0	15.5	
10	17.0	
20.1	21.0	
30	24.9	$FeSO_4 \cdot 7H_2O$
40	28.7	
50.2	32.7	
60	35.5	$FeSO_4 \cdot 4H_2O$
80	30.4	
90	27.5	$FeSO_4 \cdot H_2O$

Table 1, continued

t, °C	Amount of anhydrous salt, %	Solid phase
	$Cd(NO_3)_2$	
0	52.3	$Cd(NO_3)_2 \cdot 4H_2O$
30	58.4	
40	61.4	
59.5	76.6	
	$CdSO_4$	
0	43.0	$CdSO_4 \cdot 8/3H_2O$
20	43.4	
40	44.0	
60	45.0	
74	46.7	$CdSO_4 \cdot H_2O$
85	39.6	
100	37.7	
	KNO_2	
0	73.7	KNO_2
20	75.4	
40	77.0	
60	77.8	
80	79.0	
90	80.4	
	KNO_3	
0	11.6	KNO_3
10	17.7	
20	24.1	
40	39.1	
60	52.5	
80	62.8	
90	67.1	
100	71.1	
	$KAl(SO_4)_2$	
0	3.1	$KAl(SO_4)_2 \cdot 12H_2O$
10	4.4	
20	5.7	
30	9.2	
40	12.0	
60	26.7	
90	51.0	
100	71.4	
	$K_2Cr_2O_7$	
0	4.4	$K_2Cr_2O_7$
10	7.5	
20	11.1	
30	15.4	
40	20.6	
50	25.9	
60	31.2	
70	36.2	
80	41.1	
100	50.5	
	$KMnO_4$	
0	2.8	$KMnO_4$
10	4.0	
20	6.0	
30	8.3	
40	11.2	
50	14.4	
65	20.0	
	$K_2S_2O_8$	
0	1.62	$K_2S_2O_8$
10	2.60	
20	4.49	
30	7.19	
40	9.89	
	$KHSO_4$	
0	26.6	$KHSO_4$
20	32.7	
40	37.9	
100	54.9	
	K_2SO_4	
0	6.9	K_2SO_4
10	8.5	
20	10.0	
30	11.5	
40	13.1	
50	14.2	
60	15.4	
70	16.6	
80	17.6	
90	18.6	
100	19.4	

Table 1, continued

t, °C	Amount of anhydrous salt, %	Solid phase
	KCl	
0	22.2	
10	23.8	KCl
30	27.2	
40	28.7	
50	30.1	
60	31.3	
70	32.6	
80	33.8	
90	34.9	
100	36.0	
	$KClO_3$	
0	3.2	
10	4.8	
20	6.8	$KClO_3$
40	12.7	
60	20.6	
80	28.4	
100	36.0	
	$CaCl_2$	
0	37.5	
10	39.4	$CaCl_2 \cdot 6H_2O$
20	42.7	
40	53.5	
60	57.8	
80	59.5	
90	60.4	
100	61.4	$CaCl_2 \cdot 2H_2O$
	$Ca(CH_3COO)_2$	
0	37.4	
10	36.0	$Ca(CH_3COO)_2 \cdot H_2O$
20	34.7	
40	33.2	
60	32.7	
80	33.5	
100	29.7	
	$Co(NO_3)_2$	
18	49.7	$Co(NO_3)_2 \cdot 6H_2O$
55	61.7	
70	64.9	
91	77.2	$Co(NO_3)_2 \cdot 3H_2O$

t, °C	Amount of anhydrous salt, %	Solid phase
	$CoCl_2$	
0	30.2	
10	31.0	$CoCl_2 \cdot 6H_2O$
20	34.9	
40	39.4	
60	48.4	
80	49.0	$CoCl_2 \cdot 2H_2O$
100	50.7	
	$MgCl_2$	
0	34.5	
10	34.8	$MgCl_2 \cdot 6H_2O$
20	35.3	
40	36.5	
60	37.9	
80	39.7	
100	42.2	
	$MnCl_2$	
0	38.9	
8	38.3	
20	42.4	
30	44.7	$MnCl_2 \cdot 6H_2O$
50	49.5	
60	52.1	
80	52.0	
100	53.7	
	$CuCl_2 \times$ $\times 2NH_4Cl$	
0	22.0	
20	26.0	$CuCl_2 \cdot 2NH_4Cl \times$
40	30.5	$\times 2H_2O$
60	36.1	
80	43.4	
	$CuSO_4$	
0	12.9	
15	16.2	
25	18.7	
31	20.3	
40	22.8	$CuSO_4 \cdot 5H_2O$
50	25.1	
60	28.1	
70	31.4	
80	34.9	
90	38.5	
100	42.4	

Table 1, continued

t, °C	Amount of anhydrous salt, %	Solid phase
	Na_2SO_4	
0	4.5	
10	8.2	
15	11.7	$Na_2SO_4 \cdot 10H_2O$
20	16.1	
25	21.9	
30	28.8	
32,38	33.2	
40	32.5	
50	31.9	
70	30.5	Na_2SO_4
90	30.0	
100	29.9	
0	16.4	
10	23.4	$Na_2SO_4 \cdot 7H_2O$
16	30.9	Unstable phase
24	34.1	
	$Na_2B_4O_7$	
0	1.18	
10	1.76	
20	2.58	$Na_2B_4O_7 \cdot 10H_2O$
30	3.85	
40	6.0	
50	9.55	
60.8	16.65	
70	19.49	$Na_2B_4O_7 \cdot 5H_2O$
80	23.38	
90	28.37	
100	34.63	
	Na_2CO_3	
0	6.6	$Na_2CO_3 \cdot 10H_2O$
20	17.8	
40	33.2	
60	31.7	$Na_2CO_3 \cdot H_2O$
88.4	31.1	
	$NaHCO_3$	
0	6.45	
10	7.58	
20	8.76	$NaHCO_3$
50	12.67	
60	14.09	

t, °C	Amount of anhydrous salt, %	Solid phase
	NaCl	
0	26.21	
25	26.54	NaCl
40	26.81	
60	27.14	
80	27.65	
100	28.38	
	$NaClO_3$	
0	45.1	
15	47.6	$NaClO_3$
20	49.7	
40	56.5	
60	59.5	
80	63.6	
100	67.1	
	$NaClO_4$	
0	62.87	$NaClO_4 \cdot H_2O$
25	67.82	
50	73.26	$NaClO_4$
75	75.01	
	$NiSO_4$	
0	21.4	$NiSO_4 \cdot 7H_2O$
15	25.5	
30	29.8	$NiSO_4 \cdot 6H_2O$
44.7	32.4	
50	33.4	
60	35.4	
70	37.3	$NiSO_4 \cdot 4H_2O$
80	38.7	
99	43.4	
	$Ni(NO_3)_2$	
0	44.3	$Ni(NO_3)_2 \cdot 6H_2O$
20	49.1	
40	54.8	
55	61.1	
70	63.9	$Ni(NO_3)_2 \cdot 4H_2O$
95	77.2	$Ni(NO_3)_2 \cdot 2H_2O$

Table 1, concluded

t, °C	Amount of anhydrous salt, %	Solid phase	t, °C	Amount of anhydrous salt, %	Solid phase
	$Pb(NO_3)_2$			$Pb(CH_3COO)_2$	
0	26.7	$Pb(NO_3)_2$	30	41.02	
10	30.8		40	53.79	
20	34.3		50	68.85	
40	41.0			PbI_2	
60	46.8		0	0.044	PbI_2
80	51.8		15	0.061	
100	56.0		45	0.145	
			100	0.434	
	$Pb(CH_3COO)_2$			$PbCl_2$	
0	16.45	$Pb(CH_3COO)_2$	0	0.64	$PbCl_2$
10	22.65		15	0.91	
20	30.68		45	1.55	
25	35.26		100	3.20	

Table 1a. SOLUBILITY OF ACIDS IN 100 g OF SOLUTION CALCULATED FOR THE ANHYDROUS ACID

t, °C	Amount of anhydrous acid, %	Solid phase
	H_3BO_3	
0	2.50	H_3BO_3
10	3.52	
25	5.44	
50	10.22	
70	15.75	
100	27.52	
	$H_2C_2O_4$	
0	3.42	$H_2C_2O_4 \cdot 2H_2O$
20	8.69	
50	23.9	
70	37.9	

Table 2. DENSITY OF SOLUTIONS OF SELECTED ACIDS

Content of acids, %	Density of solutions, g/ml (15 °C)			
	H_2SO_4	HNO_3	HCl	CH_3COOH
4	1.027	1.022	1.019	1.0052
8	1.055	1.044	1.039	1.0113
12	1.083	1.068	1.059	1.0171
16	1.112	1.093	1.079	1.0228
20	1.143	1.119	1.100	1.0284
24	1.174	1.145	1.121	1.0337
28	1.205	1.171	1.142	1.0388
32	1.233	1.198	1.163	1.0436
36	1.273	1.225	1.183	1.0481
40	1.307	1.251	—	1.0523
44	1.342	1.277	—	1.0562
48	1.380	1.303	—	1.0598
52	1.419	1.328	—	1.0631
56	1.460	1.351	—	1.0660
60	1.503	1.373	—	1.0685
64	1.547	1.394	—	1.0707
68	1.594	1.412	—	1.0725
72	1.640	1.429	—	1.0740
76	1.687	1.445	—	1.0747
80	1.732	1.460	—	1.0748
84	1.776	1.474	—	1.0742
88	1.808	1.486	—	1.0726
92	1.830	1.496	—	1.0696
96	1.840	1.504	—	1.0644
100	1.838	1.522	—	1.0553

Content of acids, %	Density of solutions, g/ml (20 °C)		
	HBr	HI	HF
4	1.0269	1.0277	1.012
8	1.0568	1.0589	1.028
12	1.0883	1.0918	1.043
16	1.1219	1.1270	1.057
20	1.1579	1.1649	1.070
24	1.1961	1.2039	1.084
28	1.2367	1.2503	1.096
40	1.3742	1.4029	1.128
45	1.4446	1.4755	1.141
50	1.5173	1.560	1.155
55	1.5953	1.655	—
60	1.6787	1.770	—
65	1.7675	1.901	—

Table 3. DENSITY OF SOLUTIONS OF SELECTED BASES (15 °C)

Content of bases, %	Density of solutions, g/ml		
	KOH	NaOH	NH_3
4	1.033	1.046	0.983
8	1.065	1.092	0.967
12	1.100	1.137	0.953
16	1.137	1.181	0.939
20	1.176	1.225	0.926
24	1.217	1.268	0.913
28	1.263	1.310	0.903
32	1.310	1.352	0.893
36	1.358	1.395	0.884
40	1.411	1.437	—
44	1.460	1.478	—
48	1.511	1.519	—
52	1.564	1.560	—
56	1.616	1.601	—
60	—	1.643	—

Table 4. DENSITY OF SELECTED COMPOUNDS

Substance	Formula	Density, g/cm³	*t*, °C
Ammonium chloride	NH_4Cl	1.53	17
Antimony(III) chloride	$SbCl_3$	3.064	26
Carbon tetrachloride	CCl_4	1.632	0
Phosphorus(III) bromide	PBr_3	2.85	0
Phosphorus(III) chloride	PCl_3	1.57	0
Phosphorus(V) oxychloride	$POCl_3$	1.69	0
Silicon chloride	$SiCl_4$	1.52	0
Sodium chloride	NaCl	2.163	15-20
Sugar	$C_{12}H_{22}O_{11}$	1.588	15
Sulphur monochloride	S_2Cl_2	1.68	0
Sulphuryl chloride	SO_2Cl_2	1.67	20
Thionyl chloride	$SOCl_2$	1.675	0
Tin(IV) chloride	$SnCl_4$	2.278	0
Titanium(IV) chloride	$TiCl_4$	1.76	0

Table 5. SPECIFIC HEAT CAPACITY OF SELECTED SUBSTANCES

Substance	Specific heat capacity at 20 °C, cal/g·K	Substance	Specific heat capacity at 20 °C, cal/g·K
Aluminium	0.214	Iron	0.108
Copper	0.0915	Lead	0.0309
Glass, ordinary	0.189	Mercury	0.03325
Glass, pyrex	0.201	Platinum	0.0318
Glass, quartz	0.174	Silver	0.0559
Glass, various grades	0.2086-0.1217	Tin	0.0551
Gold	0.0309	Water	0.9985

Table 6. SELECTED ACID-BASE INDICATORS

Indicator	Concentration, %	Solvent	Colour change*	Transition range, pH
Thymol blue	0.1	20% Ethanol	Red to yellow	1.2-2.8
Methyl yellow	0.1-0.01	90% Ethanol	Red to yellow	2.9-4.0
Methyl orange	0.1	Water	Red to orange	3.1-4.4
Methyl red	0.1 and 0.2	60% Ethanol	Red to yellow	4.4-6.2
Lackmoid	0.2 and 0.5	90% Ethanol	Red to blue	4.4-6.2
Alizarin	0.02	90% Ethanol	Yellow to violet	5.5-6.8
Phenol red	0.1	20% Ethanol	Yellow to red	6.8-8.0
Thymol blue	0.1	20% Ethanol	Yellow to blue	8.0-9.6
Phenolphthalein	0.1 and 1.0	60% Ethanol	Colourless to red	8.2-10
Alizarin yellow	0.1	Water	Yellow to violet	10.1-12.1
Tropeolin O	0.1	Water	Yellow to orange-brown	11.0-13.0
Malachite green	0.1	Ethanol	Blue to colourless	11.5-14.0

* The first colour is observed at the lower pH.

Table 7. IONIZATION CONSTANTS OF WATER AT VARIOUS TEMPERATURES

Temperature, °C	*K*
25	1.8×10^{-16}
40	5.3×10^{-16}
100	9.9×10^{-15}

Table 8. IONIC PRODUCT OF WATER K_w AT VARIOUS TEMPERATURES

Temperature, °C	K_w	pH	Temperature, °C	K_w	pH
0	0.11×10^{-14}	7.48	60	9.55×10^{-14}	—
20	0.69×10^{-14}		80	25.10×10^{-14}	—
25	1.00×10^{-14}	7.00	100	55.00×10^{-14}	6.13
40	2.95×10^{-14}	—			

Table 9. DISSOCIATION CONSTANTS OF ACIDS K (25 °C)

Acid	Formula	K
Acetic	CH_3COOH	1.74×10^{-5}
Arsenic, K_1	H_3AsO_4	6.0×10^{-3}
K_2		1.05×10^{-7}
K_3		2.95×10^{-12}
Arsenous	H_3AsO_3	5.1×10^{-10}
Boric	H_3BO_3	5.8×10^{-10}
Carbonic, K_1	$CO_2(aq)+H_2O$	4.5×10^{-7}
K_2		4.8×10^{-11}
Chlorous	$HClO_2$	1.1×10^{-2}
Chromic, K_1	H_2CrO_4	1.1×10^{-1}
K_2		3.2×10^{-7}
Formic	$HCOOH$	1.8×10^{-4}
Hydrocyanic	HCN	6.2×10^{-10}
Hydrofluoric	HF	6.8×10^{-4}
Hydrogen peroxide	H_2O_2	2.0×10^{-12}
Hydroselenic, K_1	H_2Se	1.3×10^{-4}
K_2		1.0×10^{-11}
Hydrosulphuric K_1	H_2S	1.0×10^{-7}
K_2		1.3×10^{-13}
Hydrotelluric, K_1	H_2Te	2.3×10^{-3}
K_2		1.0×10^{-11}
Hypobromous	$HBrO$	2.5×10^{-9}
Hypochlorous	$HClO$	5.0×10^{-8}
Hypoiodous	HIO	2.3×10^{-11}
Iodic	HIO_3	1.6×10^{-1}
Nitrous	HNO_2	5.1×10^{-4}
Oxalic, K_1	$H_2C_2O_4$	5.6×10^{-2}
K_2		5.4×10^{-5}

Table 9, concluded

Acid	Formula	K
Periodic	HIO_4	2.8×10^{-2}
Phosphoric (ortho), K_1	H_3PO_4	7.6×10^{-3}
K_2		6.2×10^{-8}
K_3		4.2×10^{-13}
Phosphorous, K_1	H_3PO_3	1.6×10^{-2}
K_2		2.0×10^{-7}
Selenic, K_2	H_2SeO_4	1.3×10^{-2}
Selenous, K_1	H_2SeO_3	2.4×10^{-3}
K_2		4.8×10^{-9}
Silicic, K_1	H_4SiO_4	1.3×10^{-10}
K_2		1.6×10^{-12}
K_3		2.0×10^{-14}
Sulphuric, K_2	H_2SO_4	1.2×10^{-2}
Sulphurous, K_1	H_2SO_3	1.7×10^{-2}
K_2		6.2×10^{-8}
Telluric, K_1	H_6TeO_6	2.0×10^{-8}
K_2		1.1×10^{-11}
K_3		1.0×10^{-15}
Tellurous, K_1	H_2TeO_3	2.7×10^{-3}
K_2		1.8×10^{-8}

Table 10. DISSOCIATION CONSTANTS OF BASES K (25 °C)

Base	Formula	K
Ammonia solution	NH_3+H_2O	1.76×10^{-5}
Barium hydroxide, K_2	$Ba(OH)_2$	2.3×10^{-1}
Calcium hydroxide, K_2	$Ca(OH)_2$	4.0×10^{-2}
Copper(II) hydroxide, K_2	$Cu(OH)_2$	7.9×10^{-14}
Hydrazine	$N_2H_4+H_2O$	9.8×10^{-7}
Hydroxylamine	NH_2OH+H_2O	1.07×10^{-8}
Lead(II) hydroxide, K_1	$Pb(OH)_2$	9.55×10^{-4}
K_2		3.0×10^{-8}
Lithium hydroxide	$LiOH$	6.8×10^{-1}
Pyridine	C_5H_5N	1.7×10^{-9}
Silver hydroxide	$AgOH$	5.0×10^{-3}
Zinc hydroxide, K_1	$Zn(OH)_2$	4.4×10^{-5}
K_2		2.0×10^{-5}

Table 11. STABILITY OF COMPLEX IONS IN AQUEOUS SOLUTIONS

Composition of complex ions	K_{instab}	$K_{stab} = 1/K_{instab}$	t, °C
$[Ag(NH_3)_2]^+$	9.31×10^{-8}	1.07×10^{7}	30
$[Cd(NH_3)_6]^{2+}$	7.3×10^{-6}	1.36×10^{5}	30
$[Co(NH_3)_6]^{2+}$	7.75×10^{-6}	1.29×10^{5}	30
$[Co(NH_3)_6]^{3+}$	3.1×10^{-33}	3.22×10^{32}	30
$[Cu(NH_3)_2]^+$	1.35×10^{-11}	7.40×10^{10}	30
$[Cu(NH_3)_4]^{2+}$	2.14×10^{-13}	4.67×10^{12}	30
$[Ni(NH_3)_4]^{2+}$	1.12×10^{-8}	8.92×10^{7}	30
$[Ni(NH_3)_6]^{2+}$	1.86×10^{-9}	5.37×10^{8}	30
$[Zn(NH_3)_4]^{2+}$	3.46×10^{-10}	2.89×10^{9}	30
$[Ag(S_2O_3)]^-$	1.5×10^{-9}	6.66×10^{8}	20
$[Ag(S_2O_3)_2]^{3-}$	3.5×10^{-14}	2.85×10^{13}	20
$[Ag(CN)_2]^-$	8×10^{-22}	1.25×10^{21}	18
$[Au(CN)_2]^-$	5.0×10^{-39}	2×10^{38}	—
$[Fe(CN)_6]^{4-}$	1×10^{-35}	1×10^{35}	18
$[Fe(CN)_6]^{3-}$	1×10^{-42}	1×10^{42}	18

Table 12. SOLUBILITY PRODUCT K_{sp} (18-25 °C)

Substance	Formula	K_{sp}
Aluminium hydroxide	$Al(OH)_3$	1×10^{-32}
Barium carbonate	$BaCO_3$	5.1×10^{-9}
Barium chromate	$BaCrO_4$	1.2×10^{-10}
Barium sulphate	$BaSO_4$	1.1×10^{-10}
Cadmium sulphide	CdS	7.9×10^{-27}
Calcium carbonate	$CaCO_3$	4.8×10^{-9}
Calcium hydrophosphate	$CaHPO_4$	2.7×10^{-7}
Calcium hydroxide	$Ca(OH)_2$	5.5×10^{-6}
Calcium oxalate	CaC_2O_4	2.3×10^{-9}

Table 12, concluded

Substance	Formula	K_{sp}
Calcium phosphate	$Ca_3(PO_4)_2$	2.0×10^{-29}
Calcium sulphate	$CaSO_4$	9.1×10^{-6}
Chromium(II) hydroxide	$Cr(OH)_2$	1.0×10^{-17}
Chromium(III) hydroxide	$Cr(OH)_3$	6.3×10^{-31}
Copper(I) sulphide	Cu_2S	2.5×10^{-48}
Copper(II) sulphide	CuS	6.3×10^{-36}
Iron(II) hydroxide	$Fe(OH)_2$	1×10^{-15}
Iron(III) hydroxide	$Fe(OH)_3$	3.2×10^{-38}
Iron(II) sulphide	FeS	5×10^{-18}
Lead chloride	$PbCl_2$	1.6×10^{-5}
Lead iodide	PbI_2	1.1×10^{-9}
Lead sulphate	$PbSO_4$	1.6×10^{-8}
Lead sulphide	PbS	2.5×10^{-27}
Manganese sulphide (flesh coloured)	MnS	2.5×10^{-10}
Manganese sulphide (green)	MnS	2.5×10^{-13}
Mercury(II) sulphide	HgS	1.6×10^{-52}
Silver bromide	AgBr	5.3×10^{-13}
Silver chloride	AgCl	1.78×10^{-10}
Silver iodide	AgI	8.3×10^{-17}
Silver phosphate	Ag_3PO_4	1.3×10^{-20}
Silver sulphide	Ag_2S	6.3×10^{-50}
Strontium carbonate	$SrCO_3$	1.1×10^{-10}
Strontium sulphate	$SrSO_4$	3.2×10^{-7}
Zinc hydroxide	$Zn(OH)_2$	7.1×10^{-18}
Zinc sulphide	ZnS	1.6×10^{-24}

Table 13. PRESSURE OF SATURATED WATER VAPOUR IN EQUIRIBLIUM WITH WATER AT VARIOUS TEMPERATURES, DEGREES CELSIUS

Tens of degrees	Units of degrees									
	0	1	2	3	4	5	6	7	8	9
0	4.579	4.926	5.294	5.685	6.101	6.543	7.013	7.513	8.045	8.509
10	9.209	9.844	10.518	11.231	11.987	12.788	13.634	14.530	15.477	16.477
20	17.535	18.650	19.827	21.068	22.377	23.756	25.209	26.739	28.349	30.049
30	31.824	33.695	35.663	37.729	39.898	42 175	44.563	47.067	49.692	52.442
40	55.324	58.34	61.50	64.80	68.26	71.88	75.65	79.60	83.71	88.02
50	92.51	97.20	102.09	107.20	112.51	118.04	123.80	129.82	136.08	142.60
60	149.38	156.43	163.77	171.38	179.31	187.54	196.09	204.96	214.17	223.73
70	233.7	243.9	254.6	265.7	277.2	289.1	301.4	314.1	327.3	341.0
80	355.1	369.7	384.9	400.6	416.8	433.6	450.9	468.7	487.1	506.1
90	525.76	546.05	566.99	588.60	610.90	633.90	657.62	682.07	707.27	733.24
100	760.0	787.6	815.9	845.1	875.1	906.1	937.9	970.6	1004.4	1038.9

Table 14. BOILING POINT OF WATER AT VARIOUS PRESSURES

Pressure, mmHg	Boiling point, °C	Pressure, mmHg	Boiling point, °C
700	97.713	740	99.255
710	98.105	750	99.629
720	98.493	760	100.000
730	98.876	770	100.367

Table 15. CRYOSCOPIC AND EBULLIOSCOPIC CONSTANTS

Substance	Formula	Cryoscopic constant, °C	Ebullioscopic constant, °C
Water	H_2O	1.853	0.52
Chloroform	$CHCl_3$	4.9	3.8
Benzene	C_6H_6	5.065	2.61
Carbon(IV) tetrachloride	CCl_4	29.8	5.5

Table 16. TEMPERATURE OF COOLING MIXTURES CONSISTING OF SOLID CARBON DIOXIDE (DRY ICE) AND SELECTED SUBSTANCES AT 1 ATM

Substance	Formula	Temperature of mixture, °C
Ethyl chloride	C_2H_5Cl	—60
Ethanol	C_2H_5OH	—72
Ethyl ether	$(C_2H_5)_2O$	—77
Chloroform	$CHCl_3$	—77
Methyl chloride	CH_3Cl	—82

Table 17. TEMPERATURE OF COOLING MIXTURE CONSISTING OF ICE AND SELECTED SALTS (CRYOHYDRATE POINT)

Salt	Formula	Mass of salt per 100 g of ice, g	Cryohydrate point t, °C
Ammonium nitrate	NH_4NO_3	45	—17.3
Sodium nitrate	$NaNO_3$	59	—18.5
Sodium chloride	$NaCl$	33	—21.2
Calcium chloride	$CaCl_2 \cdot 6H_2O$	143	—55

Table 18. COMPOSITION AND BOILING POINT OF AZEOTROPIC MIXTURES AT 1 ATM

Mixture components	Content of first component in mixture, %	Boiling oint *t*, °C
Hydrogen bromide, water	46.85	126.0
Hydrogen chloride, water	20.30	108.6
Hydrogen iodide, water	57.00	127.0
Nitric acid, water	68.00	120.5

Table 19. COMPOSITION AND CRYOHYDRATE POINT OF COOLING MIXTURES

Salt	Mass of salt per 100 g of ice, g	Cryohydrate point *t*, °C
Sodium chloride	33	—21.2
Ammonium chloride } mixture	20	—30.0
Sodium chloride } mixture	40	
Ammonium nitrate } mixture	41.6	—40.0
Sodium chloride } mixture	41.6	
Calcium chloride hexahydrate	143	—55.0

able 20. EFFECTIVE RADII OF ATOMS AND IONS

Atomic number of element	Chemical symbol	Charge of ion	Radius of atom or ion, Å	Atomic number of element	Chemical symbol	Charge of ion	Radius of atom or ion, Å
1	H	1—	1.36	15	P	5+	0.35
		0	0.37			3—	1.86
2	He	0	1.22	16	S	6+	0.29
3	Li	1+	0.68			2—	1.82
4	Be	2+	0.34	17	Cl	7+	0.26
5	B	3+	0.20			1—	1.81
6	C	4+	0.20	18	Ar	0	1.92
		4—	2.60	19	K	1+	1.38
7	N	5—	0.15	20	Ca	2+	1.04
		3—	1.48	21	Sc	3+	0.83
8	O	2—	1.36	22	Ti	3+	0.69
9	F	1—	1.33			4+	0.64
10	Ne	0	1.60	23	V	2+	0.72
11	Na	1+	0.98			3+	0.67
12	Mg	2+	0.74			4+	0.61
13	Al	3+	0.57			5+	0.40
14	Si	4+	0.39	24	Cr	2+	0.83

Table 20, continued

Atomic number of element	Chemical symbol	Charge of ion	Radius of atom or ion, Å
	Cr	3+	0.64
		6+	0.35
25	Mn	2+	0.91
		3+	0.70
		4+	0.52
		7+	0.46
26	Fe	2+	0.80
		3+	0.67
27	Co	2+	0.78
		3+	0.67
28	Ni	2+	0.74
29	Cu	1+	0.98
		2+	0.80
30	Zn	2+	0.83
31	Ga	3+	0.62
32	Ge	2+	0.65
		4—	1.44
33	As	3+	0.69
		5+	0.47
		3—	1.91
34	Se	2—	1.93
		4+	0.64
		6+	0.35
35	Br	1—	1.96
		7+	0.39
36	Kr	0	1.108
37	Rb	1+	1.49
38	Sr	2+	1.20
39	Y	3+	0.97
40	Zr	4+	0.82
41	Nb	4+	0.67
		5+	0.66
42	Mo	4+	0.68
		6+	0.65
43	Tc	—	—
44	Ru	4+	0.62
45	Rh	3+	0.75
		4+	0.65
46	Pd	4+	0.64
47	Ag	1+	1.13
48	Cd	2+	0.99

Atomic number of element	Chemical symbol	Charge of ion	Radius of atom or ion, Å
49	In	3+	0.92
50	Sn	2+	1.02
		4+	0.67
51	Sb	3+	0.90
		5+	0.62
		3—	2.08
52	Te	4+	0.89
		6+	0.61
		2—	2.11
53	I	7+	0.50
		1—	2.20
54	Xe	0	2.18
55	Cs	1+	1.65
56	Ba	2+	1.38
57	La	4+	0.90
		3+	1.04
58	Ce	4+	0.88
		3+	1.02
59	Pr	3+	1.00
60	Nd	3+	0.98
61	Pm	3+	0.98
62	Sm	3+	0.97
63	Eu	3+	0.97
64	Gd	3+	0.94
65	Tb	3+	0.89
66	Dy	3+	0.88
67	Ho	3+	0.86
68	Er	3+	0.86
69	Tu	3+	0.85
70	Yb	3+	0.81
71	Lu	3+	0.80
72	Hf	4+	0.82
73	Ta	5+	0.66
74	W	4+	0.68
		6+	0.65
75	Re	6+	0.52
76	Os	4+	0.65
77	Ir	4+	0.65
78	Pt	4+	0.64
79	Au	1+	1.37
80	Hg	2+	1.12

Table 20, concluded

Atomic number of element	Chemical symbol	Charge of ion	Radius of atom or ion, Å	Atomic number of element	Chemical symbol	Charge of ion	Radius of atom or ion, Å
						3+	1.08
81	Tl	1+	1.49	91	Pa	4+	0.96
		3+	1.05			3+	1.06
82	Pb	2+	1.26	92	U	6+	0.83
		4+	0.76			5+	0.87
83	Bi	3+	1.20			4+	0.93
		5+	0.74			3+	1.03
		3—	2.13	93	Np	4+	0.92
84	Po	4+	1.02			3+	1.01
85	At	—	—	94	Pu	4+	0.90
86	Rn	—	—			3+	1.00
87	Fr	—	—	95	Am	4+	0.89
88	Ra	2+	1.44			3+	0.99
89	Ac	3+	1.11	96	Cm	3+	0.98
90	Th	4+	0.99				

Table 21. STANDARD ELECTRODE POTENTIALS $E°$ IN AQUEOUS SOLUTIONS AT 298 K RELATIVE TO THE STANDARD HYDROGEN ELECTRODE

Element	Reaction	$E°$, V
Ag	$Ag^{+} + e = Ag$	+0.799
Al	$Al^{3+} + 3e = Al$	—1.663
As	$H_3AsO_4 + 2H^{+} + 2e = HAsO_2 + 2H_2O$	+0.56
	$AsO_2^{-} + 2H_2O + 3e = As + 4OH^{-}$	—0.68
Au	$Au^{3+} + 3e = Au$	+1.498
Ba	$Ba^{2+} + 2e = Ba$	—2.905
Be	$Be^{2+} + 2e = Be$	—1.847
Br	$Br_2\,(aq) + 2e = Br^{-}$	+1.087
	$2HBrO + 2H^{+} + 2e = Br_2 + 2H_2O$	+1.59
	$2BrO_3^{-} + 12H^{+} + 10e = Br_2 + 6H_2O$	+1.52
	$BrO_3^{-} + 5H^{+} + 4e = HBrO + 2H_2O$	+1.49
	$BrO_3^{-} + 3H_2O + 6e = Br^{-} + 6OH^{-}$	+0.61
C	$CH_3CHO + 2H^{+} + 2e = C_2H_5OH$	+0.19
	$CH_3COOH + 2H^{+} + 2e = CH_3CHO + H_2O$	—0.12

Table 21, continued

Element	Reaction	$E°$, V
Ca	$Ca^{2+} + 2e = Ca$	−2.866
Cd	$Cd^{2+} + 2e = Cd$	−0.403
Cl	$Cl_2\,(aq) + 2e = 2Cl^-$	+1.395
	$Cl_2\,(g) + 2e = 2Cl^-$	+1.359
	$2HOCl + 2H^+ + 2e = Cl_2\,(g) + 2H_2O$	+1.63
	$HOCl + H^+ + 2e = Cl^- + H_2O$	+1.494
	$2HClO_2 + 6H^+ + 6e = Cl_2 + 4H_2O$	+1.63
	$2ClO_3^- + 12H^+ + 10e = Cl_2 + 6H_2O$	+1.47
	$ClO_4^- + 8H^+ + 8e = Cl^- + 4H_2O$	+1.38
	$ClO_3^- + 3H_2O + 6e = Cl^- + 6OH^-$	+0.63
Co	$Co^{2+} + 2e = Co$	−0.277
	$Co^{3+} + e = Co^{2+}$	+1.808
	$Co(NH_3)_6^{3+} + e = Co(NH_3)_6^{2+}$	+0.10
	$Co(OH)_3 + e = Co(OH)_2 + OH^-$	+0.17
Cr	$Cr^{2+} + 2e = Cr$	−0.913
	$Cr^{3+} + 3e = Cr$	−0.744
	$Cr^{3+} + e = Cr^{2+}$	−0.407
	$Cr_2O_7^{2-} + 14H^+ + 6e = 2Cr^{3+} + 7H_2O$	+1.333
Cs	$Cs^+ + e = Cs$	−2.91
Cu	$Cu^{2+} + 2e = Cu$	+0.337
	$Cu^+ + e = Cu$	+0.520
	$Cu^{2+} + e = Cu^+$	+0.153
	$CuCl + e = Cu + Cl^-$	+0.137
F	$F_2 + 2e = 2F^-$	+2.87
Fe	$Fe^{3+} + 3e = Fe$	−0.037
	$Fe^{2+} + 2e = Fe$	−0.440
	$Fe^{3+} + e = Fe^{2+}$	+0.771
	$Fe\,(OH)_3 + e = Fe\,(OH)_2 + OH^-$	−0.56
	$FeO_4^{2-} + 8H^+ + 3e = Fe^{3+} + 4H_2O$	+1.70

Table 21, continued

Element	Reaction	$E°$, V
H	$2H^+ + 2e = H_2$	±0.000
	$H_2 + 2e = 2H^-$	−2.251
Hg	$Hg^{2+} + 2e = Hg$	+0.850
	$Hg_2^{2+} + 2e = 2Hg$	+0.789
	$Hg_2Cl_2 + 2e = 2Hg + 2Cl^-$	+0.267
I	$I_2(c) + 2e = 2I^-$	+0.536
	$HIO + H^+ + 2e = I^- + H_2O$	+0.99
	$2IO_3^- + 12H^+ + 10e = I_2 + 6H_2O$	+1.19
	$2IO_3^- + 6H_2O + 10e = I_2 + 12OH^-$	+0.21
	$IO_3^- + 3H_2O + 6e = I^- + 6OH^-$	+0.26
K	$K^+ + e = K$	−2.924
La	$La^{3+} + 3e = La$	−2.52
Li	$Li^+ + e = Li$	−3.045
Mg	$Mg^{2+} + 2e = Mg$	−2.363
Mn	$Mn^{2+} + 2e = Mn$	−1.179
	$MnO_2 + 4H^+ + 2e = Mn^{2+} + 2H_2O$	+1.228
	$MnO_4^{2-} + 4H^+ + 2e = MnO_2 + 2H_2O$	+2.257
	$MnO_4^- + e = MnO_4^{2-}$	+0.564
	$MnO_4^- + 2H_2O + 3e = MnO_2 + 4OH^-$	+0.60
	$MnO_4^- + 8H^+ + 5e = Mn^{2+} + 4H_2O$	+1.507
N	$N_2 + 4H_2O + 2e = NH_2OH + 2OH^-$	−3.04
	$N_2 + 4H_2O + 4e = N_2H_4 + 4OH^-$	−1.16
	$N_2H_4 + 4H_2O + 2e = 2NH_3 \cdot H_2O + 2OH^-$	+0.10
	$NH_2OH + 2H_2O + 2e = NH_3 \cdot H_2O + 2OH^-$	+0.42
	$HNO_2 + H^+ + e = NO + H_2O$	+1.004
	$HNO_2 + 7H^+ + 6e = NH_4^+ + 2H_2O$	+0.864
	$NO_3^- + 3H^+ + 2e = HNO_2 + H_2O$	+0.94

Table 21, continued

Element	Reaction	E°, V
O	$O_2 + 4H^+ + 4e = 2H_2O$	+1.228
	$O_2 + 2H^+ + 2e = H_2O_2$	+0.682
	$H_2O_2 + 2H^+ + 2e = 2H_2O$	+1.776
	$O_3 + H_2O + 2e = O_2 + 2OH^-$	+1.24
	$O_3 + 2H^+ + 2e = O_2 + H_2O$	+2.07
P	$P + 3H_2O + 3e = PH_3 + 3OH^-$	—0.89
	$H_3PO_2 + H^+ + e = P + 2H_2O$	—0.51
	$H_3PO_4 + 2H^+ + 2e = H_3PO_3 + H_2O$	—0.276
	$H_3PO_3 + 2H^+ + 2e = H_3PO_2 + H_2O$	—0.50
	$HPO_3^{2-} + 2H_2O + 2e = H_2PO_2^- + 3OH^-$	—1.57
Pb	$Pb^{2+} + 2e = Pb$	—0.126
	$Pb^{4+} + 2e = Pb^{2+}$	+1.694
	$PbO_2 + 4H^+ + 2e = Pb^{2+} + 2H_2O$	+1.449
Pt	$Pt^{2+} + 2e = Pt$	—1.188
Rb	$Rb^+ + e = Rb$	—2.925
S	$S + 2e = S^{2-}$	—0.48
	$SO_4^{2-} + 4H^+ + 2e = H_2SO_3 + H_2O$	+0.17
	$H_2SO_3 + 4H^+ + 4e = S + 3H_2O$	+0.449
Sc	$Sc^{3+} + 3e = Sc$	—2.08
Se	$Se + 2e = Se^{2-}$	—0.92
	$Se + 2H^+ + 2e = H_2Se$	—0.40
	$H_2SeO_3 + 4H^+ + 4e = Se + 3H_2O$	+0.741
	$SeO_4^{2-} + 4H^+ + 2e = H_2SeO_3 + 2H_2O$	+1.15
Sn	$Sn^{2+} + 2e = Sn$	—0.136
	$Sn^{4+} + 2e = Sn^{2+}$	+0.151
	$HSnO_2^- + H_2O + 2e = Sn + 3OH^-$	—0.91
	$Sn(OH)_6^{2-} + 2e = HSnO_2^- + 3OH^- + H_2O$	—0.92
Sr	$Sr^{2+} + 2e = Sr$	—2.888

Table 21, concluded

Element	Reaction	$E°$, V
Te	$Te + 2H^+ + 2e = H_2Te$	−0.72
	$TeO_3^{2-} + 3H_2O + 4e = Te + 6OH^-$	−0.57
	TeO_2 (c) $+ 4H^+ + 4e = Te + 2H_2O$	+0.529
	H_6TeO_6 (c) $+ 2H^+ + 2e = TeO_2 + 4H_2O$	+1.02
Ti	$Ti^{2+} + 2e = Ti$	−1.63
	$TiO^{2+} + 2H^+ + e = Ti^{3+} + H_2O$	+0.10
Tl	$Tl^+ + e = Tl$	−0.34
	$Tl^{3+} + 2e = Tl^+$	+1.28
U	$U^{3+} + 3e = U$	−1.80
V	$V^{3+} + e = V^{2+}$	−0.255
	$V^{2+} + 2e = V$	−1.175
	$VO^{2+} + 2H^+ + e = V^{3+} + H_2O$	+0.337
	$V_2O_5 + 6H^+ + 2e = 2VO^{2+} + 3H_2O$	+0.958
Zn	$Zn^{2+} + 2e = Zn$	−0.763

Table 22. THERMODYNAMIC CONSTANTS OF SUBSTANCES

Substance	ΔH°_{298}, kJ/mol	S°_{298}, J/mol·K	ΔG°_{298}, kJ/mol
Ag (c)	0	42.55	0
AgBr (c)	−100.67	107.1	−97.23
AgCl (c)	−127.1	96.1	−109.8
AgI (c)	−61.94	115.5	−66.36
$AgNO_3$ (c)	−124.5	140.9	−33.6
Ag_2O (c)	−31.1	121.0	−11.3
Al (c)	0	28.3	0
Al_2O_3 (c)	−1675.7	50.9	−1582.3
$Al(OH)_3$ (amorphous)	−1276	—	—
Al_2S_3 (c)	−648.5	116.9	−637.8
$Al_2(SO_4)_3$ (c)	−3441.8	239.2	−3100.9
As (hexagonal)	0	35.6	0
AsH_3 (g)	66.4	223	68.9
B (c)	0	5.86	0
B_2H_6 (g)	38.4	232	89.6

Table 22, continued

Substance	ΔH°_{298}, kJ/mol	S°_{298}, J/mol·K	ΔG°_{298}, kJ/mol
B_2O_3 (c)	—1272.9	54.0	—1193.8
H_3BO_3 (c)	—1094.2	88.7	—968.8
Ba (c)	0	62.5	0
$BaCO_3$ (c)	—1210.8	112	—1132.2
BaO (c)	—548.1	72.0	—520.4
$Ba(OH)_2$ (c)	—941.4	108.8	—855.2
$BaSO_4$ (c)	—1458.9	132.2	—1347.9
Be (c)	0	9.5	0
$BeCO_3$ (c)	—1046.0	51.9	—965
BeO (c)	—609.2	13.8	—579.9
$Be(OH)_2$ (tetragonal)	—902.5	49.0	—814.2
$BeSO_4$ (c)	—1201.2	77.9	—1089.8
Bi (c)	0	56.9	0
BiH (g)	179.9	214.7	152.4
Br_2 (l)	0	152.2	0
Br_2 (g)	30.91	245.4	3.13
Br (g)	111.84	174.9	82.38
HBr (g)	—34.14	198.6	—51.20
HBrO (s-n)	—127.2	—	—
C (graphite)	0	5.74	0
C (diamond)	1.83	2.37	2.83
CH_4 (g)	—74.81	186.3	—50.82
C_2H_4 (g)	52.47	219.2	68.34
C_2H_6 (g)	—84.73	229.5	—32.98
HCOOH (g)	—379.0	248.7	—351.4
HCOOH (l)	—425.5	129.0	—362.2
C_2H_5OH (g)	—234.6	282.4	—168.1
C_2H_5OH (l)	—276.9	161.0	—174.2
CO (g)	—110.5	197.5	—137.1
CO_2 (g)	—393.5	213.7	—394.4
Ca (c)	0	41.6	0
$CaCO_3$ (c)	—1206.8	91.7	—1128.4
$Ca(NO_3)_2$ (c)	—744.3	—	—
CaO (c)	—635.1	38.1	—603.5
$Ca(OH)_2$ (c)	—985.1	83.4	—897.5
$CaSO_4$ (c)	—1436.3	106.7	—1323.9
Cl_2 (g)	0	223.0	0
Cl^- (s-n)	—166.8	—	—
HCl (g)	—91.8	186.8	—94.8
HClO (g)	—83.7	236.4	—70.9
HClO (l)	—34.5	188.3	84.3
Cl_2O (g)	75.7	266.2	93.4
ClO (g)	101.3	226.5	97.60
ClO_2 (g)	104.6	257.0	122.3
Cl_2O_7 (l)	251	—	—
Cl_2O_7 (g)	285	—	—
Cs (c)	0	85.23	0
Cs_2CO_3 (c)	—1136	203.9	—1053
CsOH (c)	—416.6	102.5	—371.7
Cu (c)	0	33.1	0

Table 22, continued

Substance	ΔH°_{298}, kJ/mol	S°_{298}, J/mol·K	ΔG°_{298}, kJ/mol
CuO (c)	—162.0	42.6	—129.4
$CuSO_4$ (c)	—770.9	109.2	—661.8
$CuSO_4 \cdot 5H_2O$ (c)	—2279.4	300.4	—1879.9
F_2 (g)	0	202.7	0
F^- (s-n)	—331.5	—	—
HF (g)	—270.7	173.7	—272.8
H_2F_2 (g)	—566.5	—	—
F_2O (g)	25.1	247.0	42.5
Fe (c)	0	27.2	0
Fe_2O_3 (c)	—822.2	87.4	—740.3
Fe_3O_4 (c)	—1117.1	146.2	—1014.2
$Fe(OH)_3$ (c)	—826.63	104.6	—699.65
Ge (c)	0	31.1	0
GeH_4 (g)	90.8	217.1	113.2
H_2 (g)	0	130.5	0
H^+ (s-n)	0	—	—
H_2O (g)	—241.8	188.7	—228.6
H_2O (l)	—285.8	70.1	—237.2
H_2O_2 (l)	—187.8	109.5	—120.4
I_2 (c)	0	116.1	0
I_2 (g)	62.4	260.6	19.4
I (g)	106.8	180.7	70.2
IF_5 (g)	—834.3	328.9	—763.9
IF_7 (g)	—956.0	349.8	—831.5
HI (g)	26.6	206.5	1.77
H_5IO_6 (c)	—761.5	—	—
K (c)	0	64.7	0
K_2CO_3 (c)	—1153.1	155.5	—1067.5
KH (c)	—57.8	50.2	—34.0
KNO_2 (c)	—370.6	152.1	—307.0
KNO_3 (c)	—494.5	132.9	—394.6
KOH (c)	—424.7	78.9	—378.9
Li (c)	0	29.1	0
Li (g)	159.3	138.7	126.7
Li_2CO_3 (c)	—1215.4	90.2	—1131.6
LiH (c)	—90.7	20.6	—68.7
$LiOH$ (c)	—484.9	42.8	—439.0
Li_2SO_4 (c)	—1437.2	114.0	—1322.0
Mg (c)	0	32.7	0
$MgCO_3$ (c)	—1095.9	65.1	—1012.1
MgO (c)	—601.5	27.1	—569.3
$Mg(OH)_2$ (c)	—924.7	63.2	—833.7
$MgSO_4$ (c)	—1287.4	91.5	—1173.2
Mn (c)	0	32.0	0
MnO_2 (c)	—521.5	53.1	—466.7
Mo (c)	0	28.6	0
MoO_2 (c)	—589.1	46.3	—533.2
MoO_3 (c)	—745.2	77.7	—668.1
N_2 (g)	0	191.5	0
NH_3 (g)	—46.2	192.6	—16.7

Table 22, continued

Substance	ΔH°_{298}, kJ/mol	S°_{298}, J/mol·K	ΔG_{298}, kJ/mol
N_2H_4 (l)	50.5	121.3	149.2
N_2H_4 (g)	95.3	238.5	159.1
NH_4Cl (c)	—314.2	95.8	—203.2
$(NH_4)_2Cr_2O_7$ (c)	—1807.5	—	—
NH_4NO_3 (c)	—365.4	151	—183.8
NH_2OH (c)	—115.1	66.5	—17.41
HNO_3 (l)	—174.1	155.6	—80.8
HNO_3 (g)	—135.0	266.9	—74.85
N_2O (g)	82.0	220	104.1
NO (g)	90.2	210.6	86.6
NO_2 (g)	33.5	240.2	51.5
N_2O_4 (g)	9.6	303.8	98.4
N_2O_4 (l)	—19.0	209	97.9
N_2O_5 (c)	—42.7	178.2	114.1
Na (c)	0	51.3	0
Na (g)	107.5	153.6	77.0
Na_2CO_3 (c)	—1129.4	135.0	—1045.7
NaH (c)	—56.4	40	—33.6
$NaNO_3$ (c)	—468.2	116.4	—367.4
NaOH (c)	—425.9	64.4	—379.8
Na_2S (c)	—358.6	97.9	—347.7
Na_2SO_4 (c)	—1389.5	149.6	—1271.7
O_2 (g)	0	205.0	0
O_3 (g)	142	238.8	163
P (white)	0	41.1	0
P (red)	—17.4	22.8	—11.9
P_4 (g)	59.0	279.9	24.6
PH_3 (g)	5.4	210.2	13.4
H_3PO_4 (c)	—1279	110.4	—1119.1
P_4O_6 (c)	—1640	—	—
P_4O_{10} (c)	—2984	229	—2698
Pb (c)	0	64.8	0
PbH_4 (g)	268	—	—
PbO (c)	—219.4	66.1	—189.1
PbO_2 (c)	—276.6	71.9	—218.3
Rb (c)	0	76.7	0
RbH (c)	—52.3	59	—27.4
$RbNO_3$ (c)	—495.1	155	—398.1
RbOH (c)	—418.7	92.0	—373.3
S (rhombic)	0	31.9	0
S (monoclinic)	0.4	32.6	0.2
S_2 (g)	127.5	228	78.6
H_2S (g)	—20.9	205.7	—33.8
SO_2 (g)	—296.9	248.1	—300.2
SO_3 (g)	—395.8	256.7	—371.2
SO_3 (l)	—439.0	—	—
SO_3 (c)	—	—	—
SO_4^{2-} (s-n)	—911.0	—	—
H_2SO_4 (l)	—814.2	156.9	—690.3
Sb (c)	0	45.7	0

Table 22, concluded

Substance	ΔH°_{298}, kJ/mol	S°_{298}, J/mol·K	ΔG°_{298}, kJ/mol
SbH_3 (g)	145.1	233.0	147.6
Se (hexagonal)	0	44.8	0
H_2Se (g)	33	219	19.7
SeO_2 (g)	—127	265	—132
SeO_2 (c)	—226	—	—
H_2SeO_3 (c)	—525	—	—
H_2SeO_4 (c)	—533	—	—
Si (cubic)	0	18.8	0
$SiCl_4$ (l)	—687.8	240	—
SiF_4 (g)	—1614.9	282	—1572.5
SiH_4 (g)	34.7	204.6	57.2
SiO_2 (quartz)	910.9	41.8	—856.7
Sn	0	51.5	0
SnH_4 (g)	163	229	188
SnO (c)	—286.0	56.5	—256.9
SnO_2 (c)	—580.8	52.3	—520.0
Sr (c)	0	55.7	0
$SrCO_3$ (c)	—1225.5	97.1	—1144.4
SrO (c)	—590.5	55.2	—559.8
$Sr(OH)_2$ (c)	—964.8	93.7	—876.1
$SrSO_4$ (c)	—1459.0	121.8	—1346.9
Te (hexagonal)	0	49.5	0
H_2Te (g)	99.7	228.8	85.2
TeO_2 (tetragonal)	—322	58.6	—264.6
H_6TeO_6 (monoclinic)	—1287	—	—
V (c)	0	28.9	0
V_2O_5 (c)	—1552	131	—1421
W (c)	0	32.7	0
WO_3 (c)	—842.7	75.9	—763.9

Note: The symbols g, l, c, and s-n stand for gas, liquid, crystalline, and solution respectively.

APPENDIX 2

COURSE PROJECTS IN INORGANIC CHEMISTRY

First-year students of a chemical faculty terminate their practical course with an experimental course project whose topic (the synthesis of an inorganic compound) is given to each student at the beginning of the second semester.

While working on this project, a student should look through the reference books and journals (mainly referative ones) recommended by his instructor to acquaint himself with the most important physicochemical properties and ways of preparing the given compound. After compiling a review of the literature, the student performs the relevant experiment in the laboratory for practical work or in the scientific laboratory of the department.

After completing the experiment and handing in the synthesized substance to his instructor, the student should write a report on the project using the form adopted for a thesis. The project is defended during the last lesson of the class in the presence of the class instructors and members of the department's methodological committee. Each student reports for five to seven minutes on the results of his work and answers the questions he is asked.

When rating a student's work, the instructors should take into consideration the results of the experiment, the record of the work, the student's ability to discuss the purpose and the performing of the experiment, and the student's attitude to carrying out the course work. The mark for the project is entered in the student's record book. The best works are included in the competition of projects organized by the department of inorganic chemistry.

This project in inorganic chemistry is of major significance because for many students it is the first work containing an element of research where the student can show his initiative.

APPROXIMATE PROJECT TOPICS

1. Preparation of titanium tetrabromide.
2. Preparation of cerium molybdic acid and its salts.
3. Preparation of potassium hexachlorotellurate.
4. Preparation of cobalt complex compounds.
5. Preparation of phosphonitrile chloride.
6. Preparation of certain magnesium alcoholates.
7. Preparation of potassium and sodium tetrathionates.
8. Preparation of chromium(III) ammonia complexes.
9. Preparation of manganese(II) and manganese(III) nitrilotriacetates.
10. Preparation of nickel(III) ethylene diaminetetraacetates.
11. Preparation of silico-10-tungstic acid.
12. Preparation of telluric acid.
13. Preparation of sodium tetrafluoborate.
14. Preparation of rare-earth element complexes with ascorbic acid.
15. Preparation of samarium tri- and dichloride.
16. Preparation of sodium and potassium fluoberyllates.
17. Preparation of lithium borhydride.
18. Preparation of tantalum(V) chloride.
19. Preparation of tellurium(IV) halides.

One of the syntheses described in this book can also be the topic of a course project.

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